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Formation of Photochemical Aerosols

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16 ABSTRACT

The objective was to develop a better understanding of smog aerosol formation with particular reference to haze in the Southern California area. This study combined laboratory work with ambient air studies. Counting of particles by light scattering was the principle physical technique while infrared analyses was the major source of chemical information. A new reflectance spectroscopy technique was also developed.

Infrared spectra of ambient aerosols have bands assigned to sulfate, nitrate, ammonium, and water which are completely removed by water washing of the sample but not by benzene. Synthetic aerosols generated by mixing ammonia with sulfuric and nitric acids produce similar spectra.

Many ambient aerosol particles are hygroscopic or deliquescent so that they swell as the relative humidity increases and shrink as it decreases. This readily explains the heavy haze seen at high humidity days.

A variety of reaction products ($SO_4^=$, NO_3^-, organics) can potentially fulfill the requirement of water solubility and hygroscopicity to contribute to haze and loss of visibility. It is concluded that direct control of aerosol emissions will not markedly improve visibility in Southern California.

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FORMATION OF PHOTOCHEMICAL AEROSOLS

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ABSTRACT

Although aerosol is the most readily apparent symptom of photochemical smog because of its affect on visibility, its scientific study was long neglected in favor of the more pressing questions of eye irritation, plant damage, and health hazards. The early reports by Haagen-Smit suggested that visible haze might be due to sulfuric acid formed by atmospheric oxidation of sulfur dioxide (1). He also noted that the rapid reaction of ozone with olefin (at high concentrations) produced a dense "fog." Since this reaction system also caused eye irritation and plant damage it seemed fair to regard it as a good synthetic or laboratory smog. The relative importance of the sulfuric acid and ozone/olefin aerosols was not studied for many years nor has there been a good quantitative, realistic simulation in the laboratory of smog aerosol formation.

The present project had as its general objective a better understanding of the smog aerosol with particular reference to haze as it is observed in inland (receptor) areas of Southern California. It combined laboratory studies with ambient air studies in the belief that full understanding requires a reconciliation of the two. Counting of particles by light scattering was the principle physical technique while infrared analysis was the major source of chemical information. A new technique of reflectance spectroscopy was developed for this purpose. Spectra were recorded by reflectance through samples deposited by impaction on noble metal targets. This technique requires small samples and has the unique advantage of distinguishing between sulfuric acid and other sulfates since the sample has no opportunity of reacting with anything but itself. This new technique is regarded as one of the most important accomplishments of this project.

Infrared spectra of ambient aerosols have bands assigned to sulfate, nitrate, ammonium and water which are completely removed by water washing of

the sample but not by benzene washing. A synthetic aerosol generated by mixing ammonia with sulfuric and nitric acids produced a very similar spectrum. One pair of ambient samples gave spectra which looked more like sulfuric acid than sulfates. The larger particles gave a 10 micrometer band, insoluble in water and benzene, which is attributed to soil dust. Few samples showed any OH band of organic material and no carbonyl band was identifiable. Synthetic organic aerosols either from ozone/olefin or olefin/nitrogen oxide reactants do show such bands but they are not water soluble. It also appears difficult to produce significant amounts of organic aerosol from realistic levels of hydrocarbon/NO_x mixtures. It was concluded that a much more sophisticated apparatus would be necessary to attain a good simulation of photochemical aerosol formation. Long reaction times at low reactant concentrations are required and the rate of loss of aerosol to the wall must be minimized. This calls for a small surface-to-volume ratio. While it is clear that organic material makes a contribution to aerosol it is still not possible to uniquely characterize it as to source and history or in its contribution to visible haze.

Many ambient aerosol particles are hygroscopic or deliquescent so that they swell as the relative humidity increases and shrink as it decreases. This readily explains the heavy haze often seen when humidity is high but oxidant is low as in the early morning hours. Frequently the visibility improves as the temperature rises and the relative humidity falls during the forenoon.

A variety of reaction products ($SO_4^=$; NO_3^-; organics) can potentially fulfill the requirement of water solubility and hygroscopicity (or deliquescence) to contribute to haze and loss of visibility. The relative importance to haze of these species may well be different at different times and places. Also still not settled are the exact sequence of reactions which produce these aerosol products. These are matters of importance in control strategy and not just of scientific curiosity. Abatement of aerosol might be achieved either by control of precursors (for example, sulfur in fuels) or control of the oxidation process which produces aerosol products. At least it has become clear that control of direct aerosol emissions will not markedly improve visibility in inland Southern California.

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SECTION I

INTRODUCTION

Development of a complete understanding of the aerosol component of photochemical smog has attracted increasing attention in recent years. In addition to its health hazards, aerosol also causes a prominent loss of visibility which is evident to every citizen. In inland Southern California visibility is often reduced to a few miles even when the humidity is only 30-40%. Visibility impairment is quite evident even when smog is light as judged by other symptoms. This project had the objective of clarifying the nature of this smog manifestation with particular reference to the aerosol which occurs in Riverside, California. The first results were described in two papers--a short one in 1970[1] and a longer one in 1972.[2] It was shown that "unreacted" air polluted with car exhaust causes very little visibility loss even though there are large numbers of countable particles.

It was argued in ref. (2) that atmospheric oxidation of sulfur dioxide could produce substantial visibility loss since sulfuric acid would condense to produce particles of a size most effective for scattering light. This is certainly not a new idea; the earliest of Haagen-Smit's papers suggest it (without detailed proof).[3] Even the sulfur dioxide derived from auto exhaust would produce substantial visibility loss if a large portion of it were photooxidized to sulfuric acid as shown in Table I. The high oxidant levels of inland Southern California show that the photochemical reaction is more advanced in those areas than in most places. Enhanced photochemical aerosol can therefore be expected. Laboratory studies have shown that sulfur dioxide can be oxidized to sulfuric acid under simulated atmospheric conditions (1, 2 and references therein), but some hydrocarbon/nitrogen oxide mixtures will produce an organic aerosol in the absence of sulfur dioxide. It has proven difficult to determine the relative contributions of these two distinct types of aerosols in real polluted air. The problem is

TABLE 1. AEROSOL FORMATION FROM AUTO EXHAUST BY PHOTOCHEMICAL FORMATION OF SULFURIC ACID

1.	Gasoline combustion	15	0.065 0.065 sulfur by weight 15 grams exhaust/gram fuel
2.	Exhaust gas dilution	19,000	0.0065 - 50 ppm S by weight = 50 ppm SO_2 by volume
3.	Polluted air photooxidation with HC/NO_x	5 %	0.004 ppm SO_2 Assume 100% conversion
4.	Sulfuric acid absorption of moisture at 40% RH	5 %	0.004 ppm H_2SO_4 = 16 micrograms/meter^3 32 micrograms of 50% H_2SO_4/meter^3
5.	Smog aerosol		360 million droplets (0 0.3 - 1.0 micron)/meter^3

complicated by the fact that the respective weights of various aerosol components are not necessarily a reliable guide to the contributions to visibility loss. Many different kinds of carbon, both inorganic and organic (even biological) can contribute to aerosol weight so that measurement of "benzene soluble" or total organic carbon still does not quantify the contribution to light scattering nor can it distinguish between primary organic aerosol (for which there are many sources) and photochemically formed organic aerosols. This field of study has been very active as is shown by the list of recent references dealing with some aspects of aerosol as related to visibility (see Bibliography).

Since Riverside has frequent episodes of medium to heavy smog including heavy haze it is an ideal place for this study. A primary aim was to use the same techniques on both natural and synthetic aerosols. One of the difficult problems, not only in aerosol studies but in any laboratory study of smog, is in establishing the importance of any laboratory finding in the real atmosphere. This gap can only be bridged by achieving quantitative and consistent results in both settings.

SECTION 2

METHODS

The basis of this aerosol study was to apply the same aerosol measurement techniques to ambient air in Riverside and to aerosols generated in the laboratory. This approach is potentially much more informative than either kind of study alone. The aim is to generate in the laboratory an aerosol which matches as closely as possible the properties of the ambient aerosol. Two principal methods of aerosol analysis were used in this study, one to provide physical information and one to provide chemical information.

PARTICLE COUNTING

Particle size distributions were measured with a Bausch and Lomb 40-IA forward-scattering particle counter. This can be used to count particles larger than 0.3 μ (polystyrene equivalent) diameter. As supplied by the manufacturer, this counter has a lower-limit discriminator which can be set to any of eight levels. It then provides a count of total particles larger than the given diameter. Thus, a size spectrum can be obtained by switching the counter from one minimum diameter setting to another. This has a disadvantage, especially when working with ambient samples, that the count for each size is made on a different sample of air, and there is no way to be certain that the particle size distribution remains constant for the approximately 16 min required to measure one spectrum. Another disadvantage of this counting system is that when measuring particles of large size, which are very few in number, all the information about the smaller diameter particles is being wasted. Within these limitations, this counter appears to be an accurate and reliable means of estimating the number of particles in various size ranges in laboratory aerosols and in ambient aerosols. It requires a rather small flow rate which is one of its major advantages for use in laboratory studies, since laboratory reactors provide limited volumetric flow. The

counter is calibrated in terms of polystyrene equivalent diameters. Whatever the ambient aerosol is, it is certainly not polystyrene. It may much more likely be sulfuric acid. To make a more realistic size discrimination, the polystyrene equivalent diameters were corrected to sulfuric acid equivalent diameters for some studies. Plots of scattered light derived from Martens and Keller[6] were used for this purpose as given in Figure 1. The counter was used to count aerosols formed in the laboratory reactor, and to count ambient aerosols under various weather and pollution conditions.

To make full use of the information provided by this counter its electronics were completely rebuilt to provide an input for a 200-channel pulse-height analyser. This turned out to be a rather major operation but it was successfully completed. This permitted simultaneous measurement of particles of all sizes which assures spectrum consistency and also permits much finer resolution. All the data in this report were completed before this modification was complete.

INFRARED ANALYSIS

To provide chemical information on these synthetic and natural aerosols the special impactor shown in Figure 2 was developed. It provides a spot sample of aerosol which matches the geometry of the entrance beam of a small infrared spectrophotometer (Perkin-Elmer 137B) (1.5 × 1.5 mm). This permits the recording of transmission spectra. Three versions of this scheme have been explored. In the first version infrared transmitting targets such as BaF_2, BaF_2/CaF_2 (T12) and TlBr/TlI (KRS-5) were used. These crystals not only transmit infrared but they are also insoluble in water. The KRS-5 crystal covers the 2-15 micrometer wavelength range whereas the other two are limited at the long wavelength end. Good spectra can be obtained within these limits although ambient air samples etch the targets to form a scar which must be polished out after each use. This etching implies that the samples react with the target and must themselves therefore be changed. This is consistent with the identification of strong acids as components of the aerosol. This result prompted the investigation of the use of noble metals as targets combined with reflectance spectroscopy for analysis.

To obtain a good reflection spectrum it is necessary to ensure that most of the infrared beam pass through the sample. This requires that the source

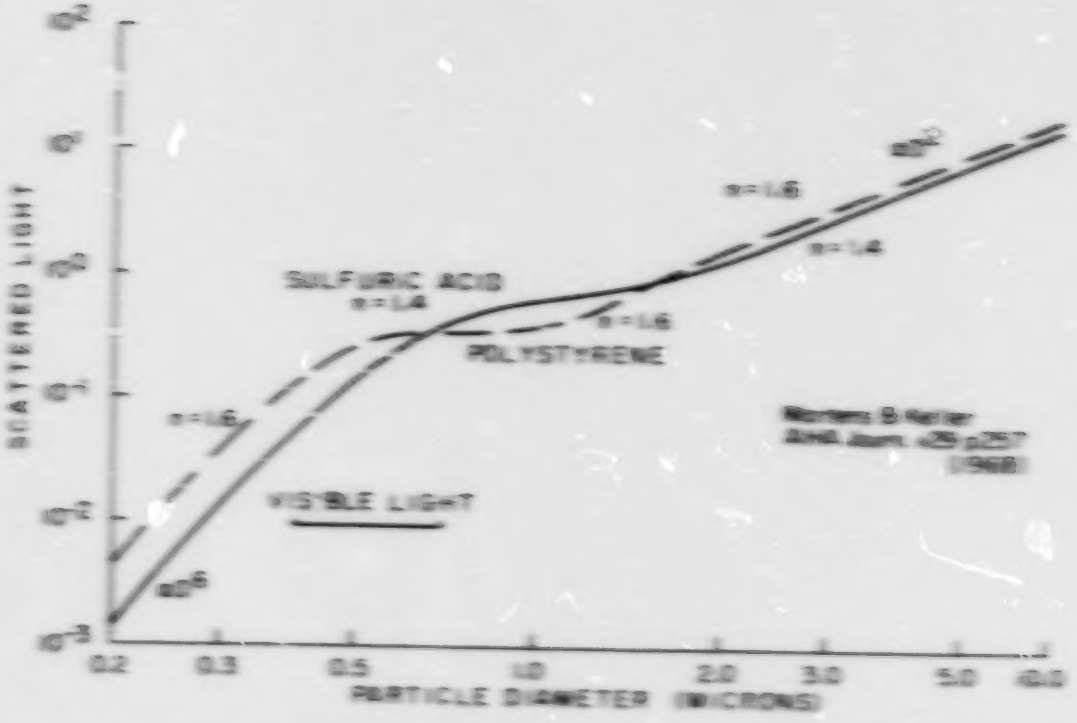


Figure 1. Correction of Bertana and Kellner[4] light scattering function for index of refraction of 1.6 for polystyrene to sulfuric acid index of 1.4.

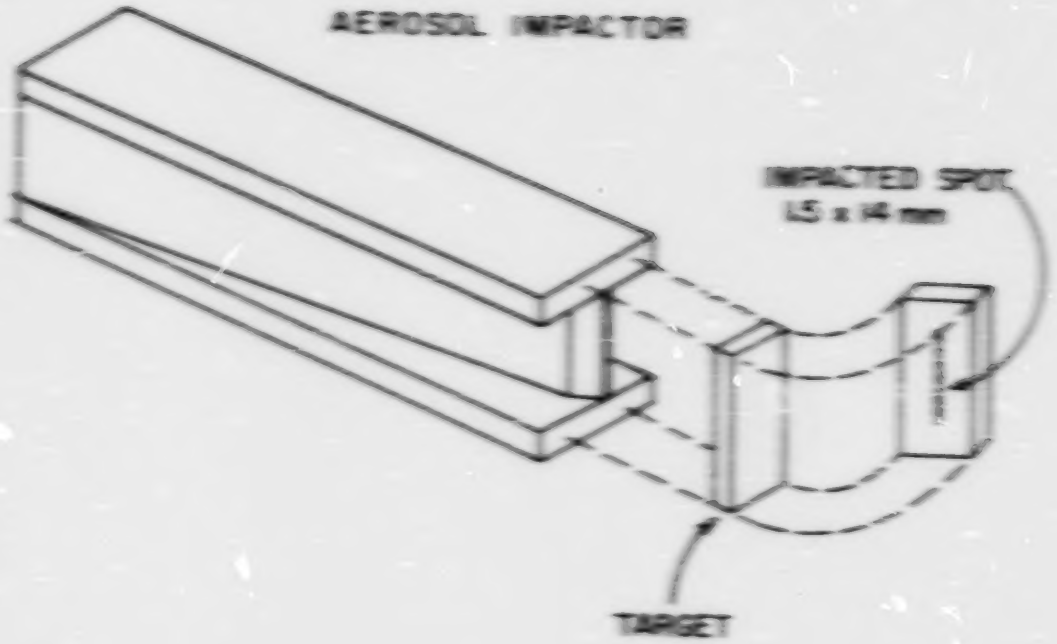


Figure 1. Aerosol impactor which produces a spot on either an infrared transparent target or a corrosion resistant metal plate.

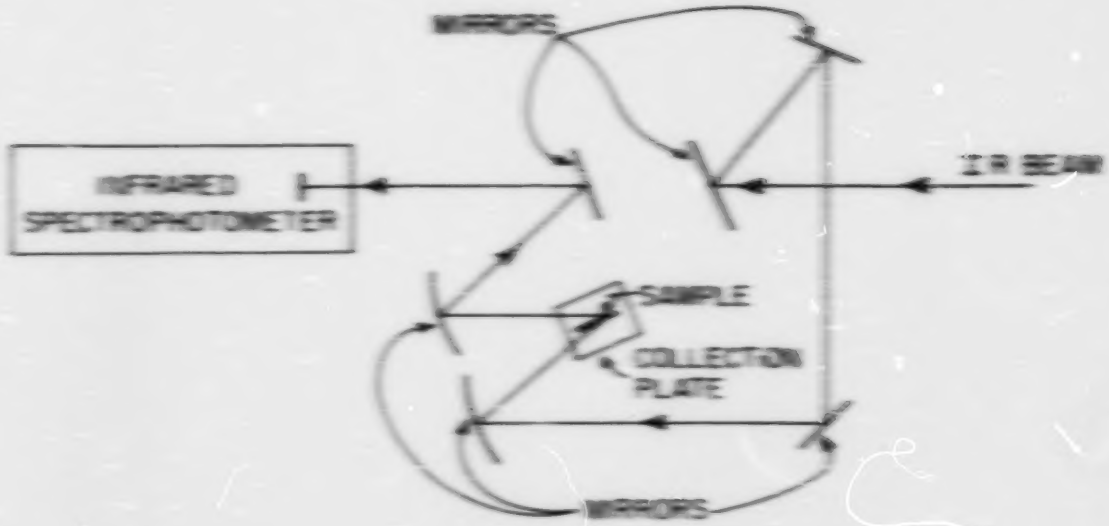
of radiation be imaged sharply on the sample and that this image in turn be sharply imaged in the entrance slit of the spectrometer. Results were not satisfactory with an ordinary reflectance attachment but a microspecular reflectance attachment (Barnes Engineering Co., Model No. 126) yielded strong reflectance spectra (Figure 3). This accessory places a 1:1 reduced image of the source on the reflective sample surface. This would make it possible to use an impactor of shorter slit length which would in turn permit reduction in the sample flow rate by a factor of three. This would be particularly advantageous in sampling from laboratory reactors. It might permit reduction of the sample size to 100 liters for heavy aerosols. Such a small impactor has not yet been constructed.

Impactor efficiency was estimated by counting the particles in a sample of air which had been passed through the impactor using the system shown in Figure 4. A 35-liter steel tank was inserted in the line between the impactor and the vacuum pump. In this way the tank could be flushed with impactor effluent. The slit widths, spacings and flow rates tested are listed in Table 2. While the tank was purging, the size distribution of the aerosol

TABLE 2. IMPACTION EFFICIENCY OF THE IMPACTOR AT VARIOUS SLIT WIDTHS, SPACING AND FLOW RATES

		% Impacted						
Slit width (mm)		0.76	0.76	0.76	1.3	1.3	1.3	0.38
Spacing (mm)		0.25	0.25	0.51	0.25	0.51	0.65	0.38
Flow rate (l/min)		19	28	28	28	28	28	28
Aerosol size μ	0.3-0.5	27	35	45	39	-15	8	87
	0.5-1.0	50	59	73	67	51	44	95
	1.0-1.8	64	69	84	71	85	68	94
	1.8-2.0	86	81	100	86	83	71	100
	2.0 +	100	100	100	100	100	100	100

in the ambient air was measured with the Bausch and Lomb 40-A particle counter. Then the pump was stopped and the aerosol in the tank counted with the results. For most sampling the first stage had a slit 1.3 cm wide at a target distance



OPTICAL DIAGRAM
MODEL 126
MICRO SPECULAR REFLECTANCE

Figure 1. Reflectance attachment which places a 1:1 reduced image of the source on the sample (which is vertical rather than horizontal as shown here).

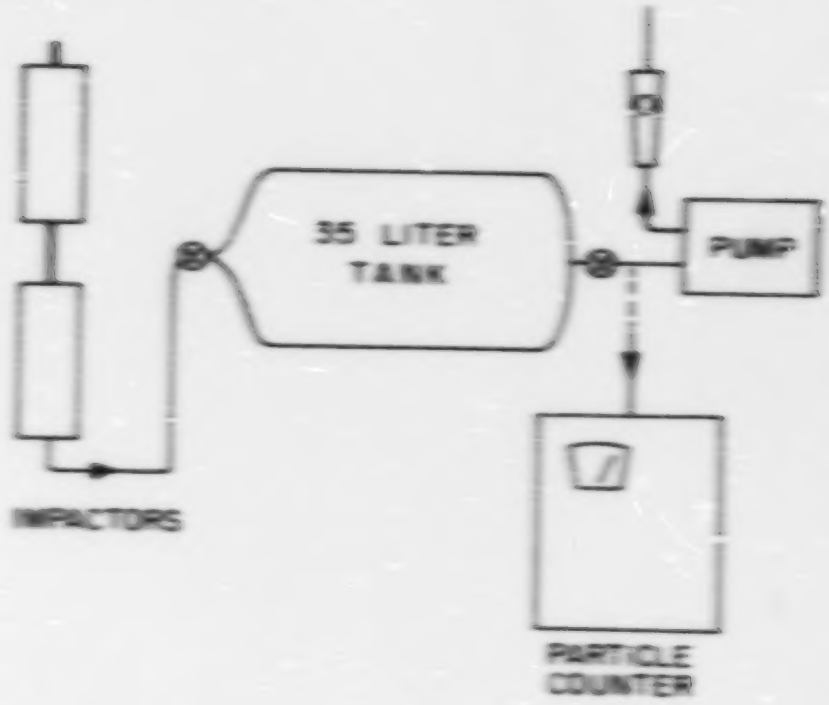


Figure 4. Arrangement for estimating the two-stage impactor's efficiency in collecting ambient aerosol.

of 0.65 mm while the second stage had a width of 0.4 mm and a spacing of 0.4 mm. Balanced against its obvious shortcomings this procedure has the advantage of referring the test to the sample, ambient air, of immediate interest.

Most of the best data were obtained using a two-stage impactor designed to cut the sample at about 1 or 2 microns diameter. This should put the windblown dust on the first stage and most of the photochemically generated particulate on the second stage. A flow rate of 28 liters/min was selected. This gives a strong spectra on both stages of the impactor in two hours sampling for moderate smog conditions. Shorter sampling times can be used for heavier ambient aerosols. Hundreds of spectra were obtained with this system.

To provide additional information, procedures were devised for treating the samples with moist air or dry air while recording the spectrum. Samples were also washed with various solvents taking care to remove the sample only by solution rather than by mechanical flushing. The spectrum could then be recorded again.

Two additional techniques of aerosol sampling for infrared examination were tested during the course of this project. These were thermal precipitation and the LEAP spinning disk sampler. The thermal precipitator operates at a very low flow rate and therefore requires a long sampling time. It has the advantage of collecting very small particles. Even twenty-four-hour samples did not suffice to collect a sample adequate for infrared analysis, however. The LEAP sampler handles a very large flow of air but produces an aqueous solution or suspension of the aerosol. Trial experiments with this sampler were not very informative.

One other program of infrared study of aerosol samples has been carried out at Argonne National Laboratories by Cunningham and associates.[5,6] They collected Lundgren impactor samples which were transferred into KBr powder and pressed into pellets for infrared examination. Although Fourier transform spectroscopy was used, their published spectra did not use high resolution, probably because no fine structure was present in the spectrum. Generally speaking, these spectra are similar to the ones generated in the present project and were interpretated in terms of sulfate/nitrate with little

evidence of organic CH bands. Aside from the extra procedure of preparation of the pellet this method has the disadvantage of allowing interaction of sample with the salt (as compared to the reflection method). The advantage is in the potential for a quantitative analysis.

SPECTRAPHONE

Although several different methods of aerosol sampling have been used in this and other projects no one of them is ideal. A system which would permit analysis of the aerosol phase without separation from the gas would eliminate many uncertainties in the sampling process. Accordingly, schemes for recording the spectrum of the aerosol phase directly have been explored in considerable detail. The spectraphone concept, based on heating of a gas by absorption of radiation in the characteristic wavelength bands, was investigated in a detailed paper study. Since gases as well as particulates absorb radiation, a subtraction technique must be used to extract the desired spectral information. The details of the design analysis are being given in another report (in progress).

GENERATION OF SYNTHETIC AEROSOLS

Several different methods for generating synthetic aerosols and obtaining their spectra were used during the course of this project. These ranged from a laboratory flow tube reaction to vehicle engines of various types. Two types of "atomizers" were also used to make aerosols for spectra and some spectra of inorganic aqueous solutions were recorded by conventional techniques.

Photoreactors

A tubular flow reactor, which has been used for a number of years to study simulated photochemical reactions,[7] was used for this study. It is made from sections of borosilicate glass drain line 15.24 cm (6 in) in diameter in the form of a U-tube, each arm of which is about 3.05 meters (10 ft) long (see Figure 5). The total volume is about 140 liters. With a flow rate of 2.15 liters/min the residence time in the flow reactor is 1 hr. The humidity in the incoming air was maintained at a standard level with an ice bath humidifier. Pollutants are then added at a low concentration and the mixture

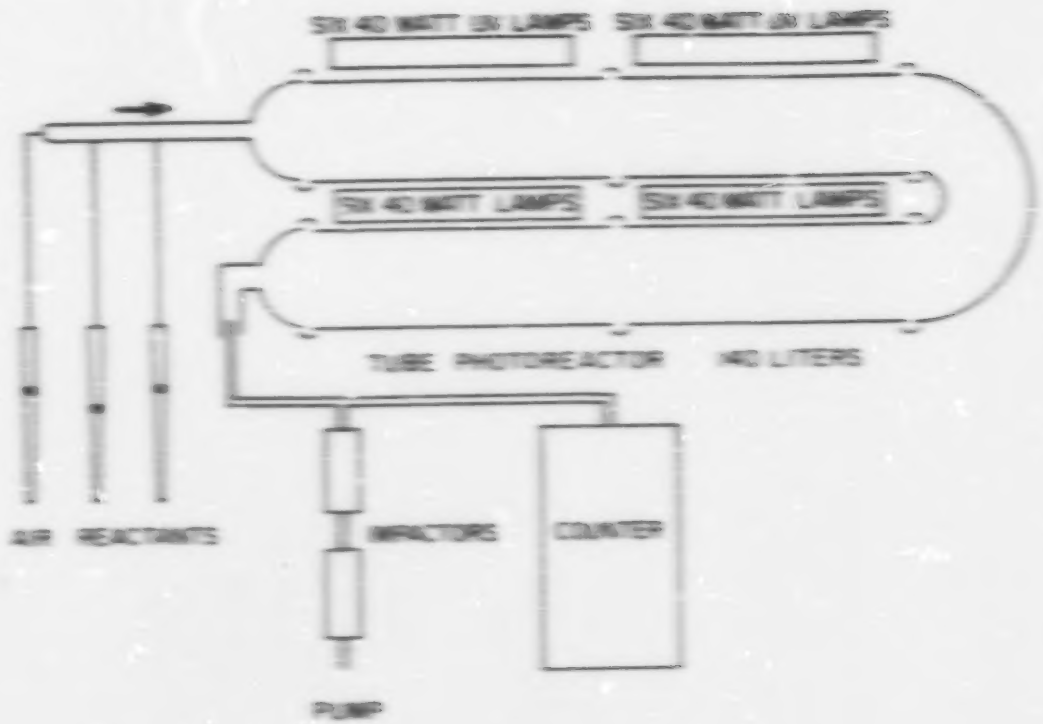


Figure 1. Tube flow photoreactor.

passed into the reactor. Each 5-ft section of the reactor is surmounted by six blacklight fluorescent lamps to provide simulated sunlight. The effluent from the reactor can be analyzed for chemical products or for aerosol.

In addition to aerosols generated chemically either by photolysis of hydrocarbon/nitrogen oxides/sulfur oxides mixtures or hydrocarbon/nitrogen oxides mixtures,[1] synthetic inorganic aerosols were also made in the tube photoreactor. Sulfuric acid aerosol was prepared by vaporizing fuming sulfuric acid into a stream of air. A particle size distribution obtained for a typical synthetic sulfuric acid aerosol as it entered the tube reactor and as it left the tube reactor are shown in Table 3. From these data it

TABLE 3. SULFURIC ACID AEROSOL IN TUBE PHOTOREACTOR

Diameter		Particles/ft^3 Input	Output
Microns	0.3	6.397×10^5	6.004×10^5
0.3	0.5	1.430×10^6	1.414×10^5
	1.0	6.254×10^5	0.236×10^5
	1.8	0	0
		Calculated $\mu g/m^3$	
1.0 < D ≤ 0.3			11.7
1.8 < D ≤ 1.0			5.3
		Equivalent ppb SO_3	
1.0 < D ≤ 0.3			2.9
1.8 < D ≤ 1.0			1.4
Measured SO_3 ppb		620	660

appears that there was very little loss of aerosol in the one hour time of residence in the flow tube. For some unknown reason the conductivity analyser indicated a far higher H_2SO_4 concentration than the particle count. We cannot, of course, be sure that the particles leaving the reactor were the same as those entering the reactor since only a portion of the total size spectrum is counted and particles too small to be measured in the reactor input may well have coagulated in passage through the tube, and larger particles may

have fallen out during passage through the tube. Sampling from this reactor with the impactors presented some difficulty since the flow from the reactor was less than one tenth of that needed for impaction. The scheme shown in Figure 6 was developed to solve this problem. The reactor effluent was diluted with filtered compressed air and the diluted aerosol passed through the impactor. A stirred flow bottle reactor shown in Figure 7 was also used for some experiments.

Aerosol Generators

To generate test aerosols for impaction spectra the nebulizer shown in Figures 8 and 9 was constructed. It produces a stream of airborne particles from either a polystyrene latex emulsion or from a water solution of soluble salts. Since the ambient aerosol has a large component of aqueous droplets, some reference spectra were also obtained by pressing water solutions between KRS-5 plates. The water absorptions are so strong that no spacer could be used; only the residual film between the two infrared windows.

Auto exhaust particulate was sampled using a dilution system similar to that shown in Figure 6. These experiments were qualitative and only intended to provide reference spectra for the ambient air samples.

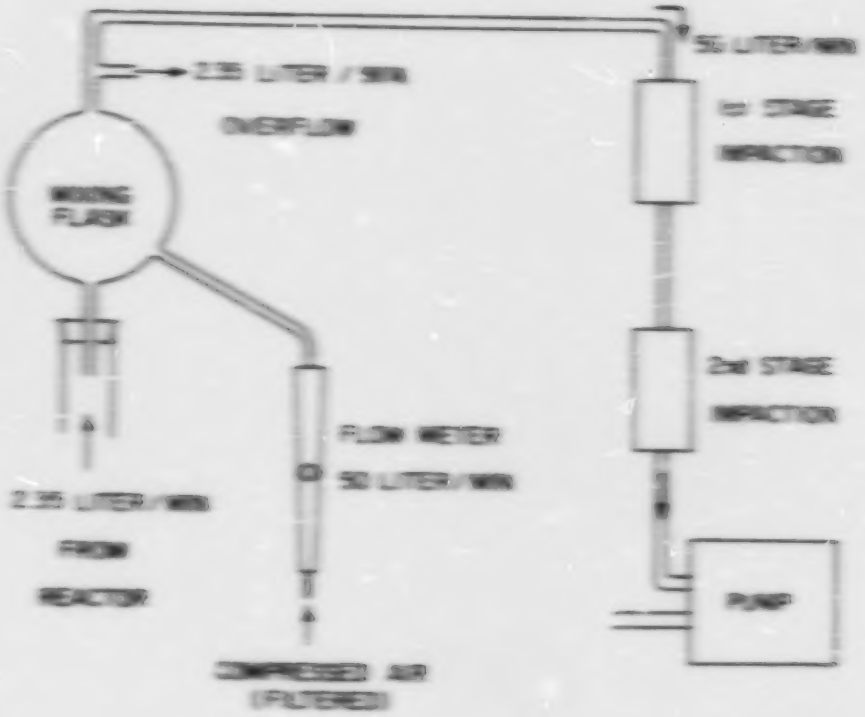


Figure 6. Dilution apparatus for sampling from the tube flow photoreactor.

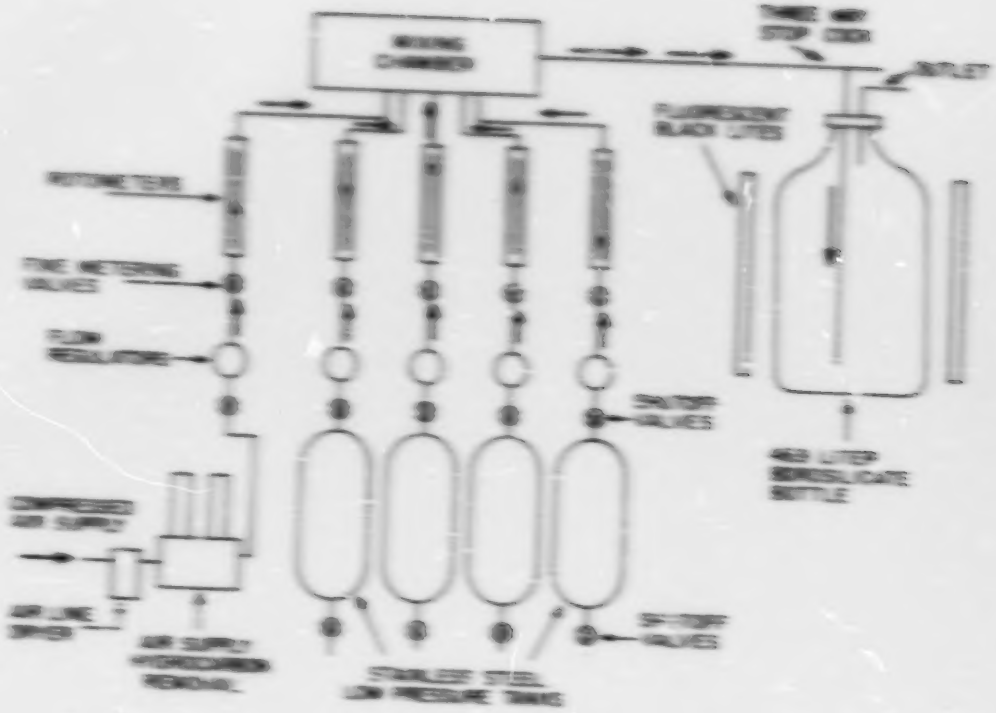


Figure 1. Skirted flow photoreactor.

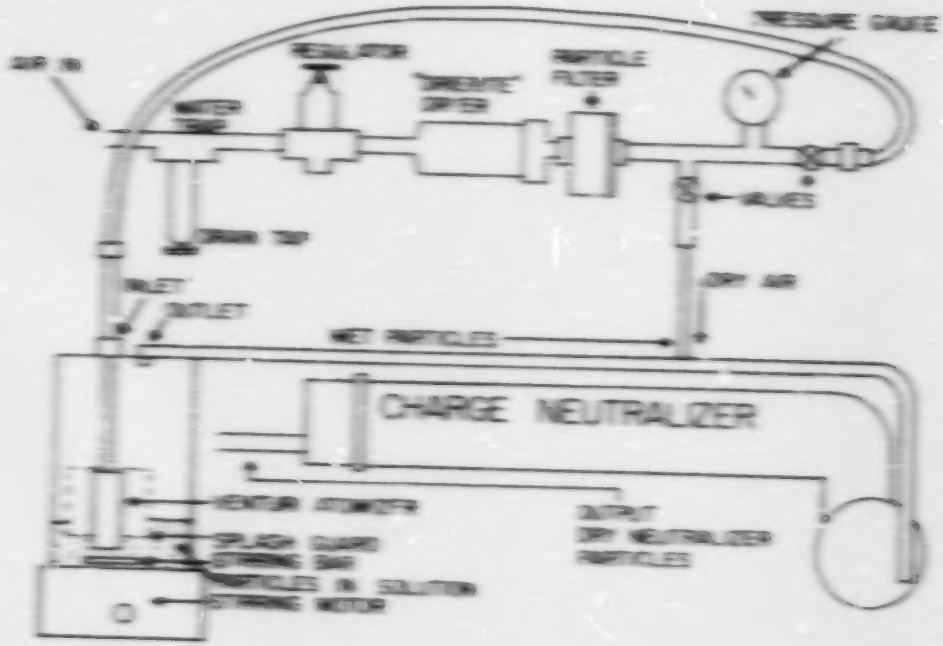
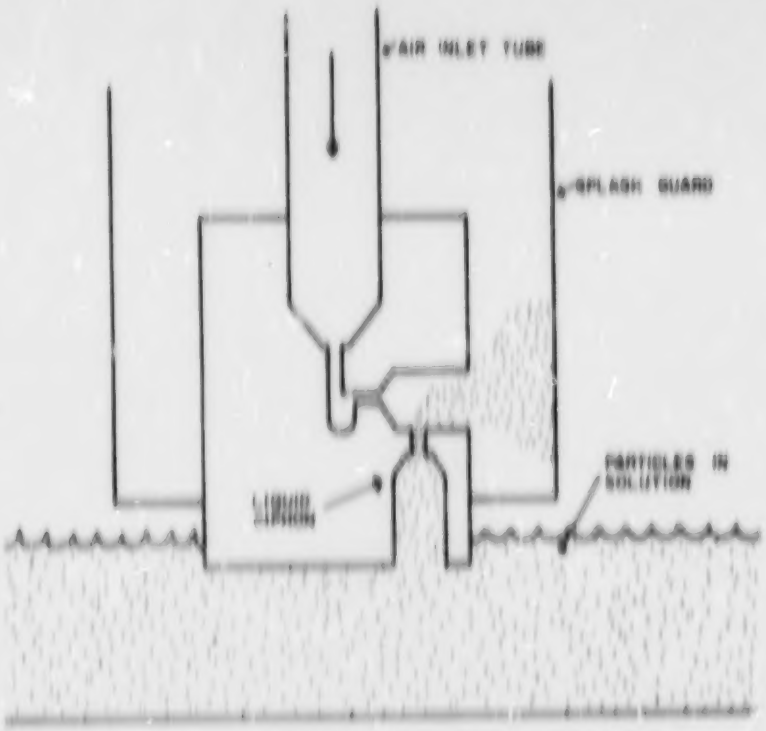


Figure 8. Apparatus for generation of aerosols for impaction to make reference spectra.



VENTURI ATOMIZER

Figure 9. Atomizer section of particle generator.

SECTION 3

RESULTS

Heavy photochemical smog gives about 10^7 particles/ft^3 (350 particles/cm^3) countable with the Bausch and Lomb instrument (larger than 0.3 micrometer diameter). The number of course, falls off steeply with increasing diameter as shown in Figure 10 which compares a day with a very high oxidant (0.65 ppm) to three days of distinctly different weather and with much better visibility. In each of these cases there were sufficient particles to provide condensation nuclei. One of the commonest questions posed by laymen about smog aerosol is "How much of this is smog and how much is fog?" or, when the oxidant and sunshine are low but the visibility is impaired, "But this isn't smog is it, isn't it just haze?" The answer seems to be that the aerosol from smog persists even when the oxidant is low or after the oxidant has been destroyed by NO emissions. Cases can be cited of equivalent or higher humidity but much better visibility in Riverside and elsewhere. The "haze" which persists when oxidant and photochemistry are minimal must be due to residual pollution which can impair visibility noticeably, especially if the pollutants are hygroscopic and if the relative humidity is high. They cannot be explained by lack of condensation nuclei; these are never in short supply in the real atmosphere. But high humidity alone will not produce a visible haze. The lowest curve in Figure 10 was taken on an overcast, rainy day when the humidity was 78% (much higher than typical smog) (Temp. 61°F, wet bulb 57°F) but the visibility was unimpaired. Any haze due to natural causes should have been visible on such a day.

Santa Ana wind episodes produce some of the best visibility this area ever enjoys. Although under extreme conditions these winds from the north and northeast can create a very heavy loading of sand and dust, milder winds produce lower counts as shown in Figure 10. A few times each year, especially in winter, a mild Santa Ana condition is followed by a calm, cloudless night

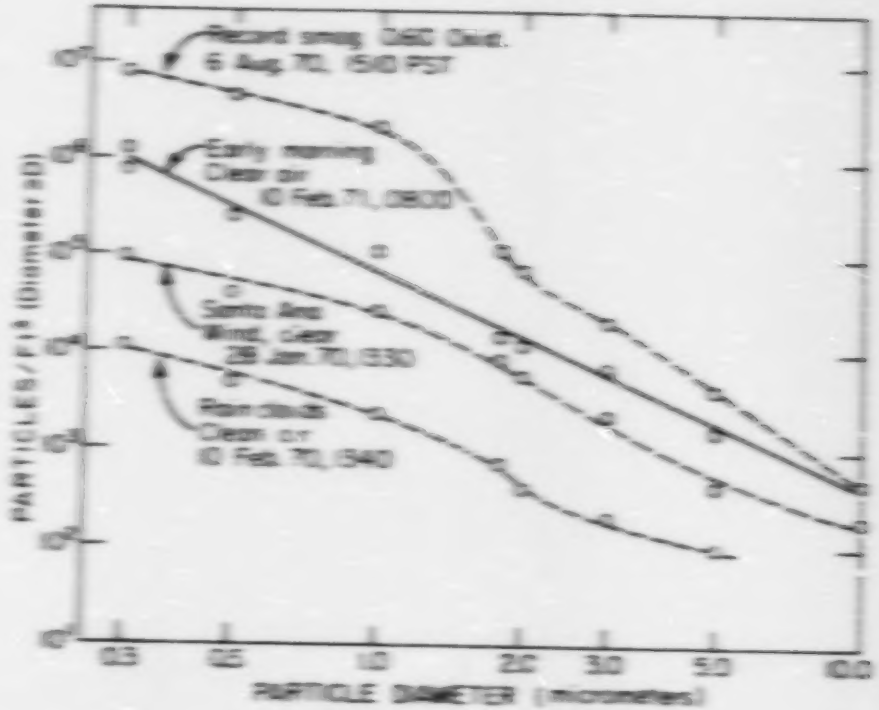


Figure 10. Aerosol size spectra (cumulative) for four distinctly different weather conditions.

which produces a strong but shallow radiation inversion at dawn. If radiation cooling of the surface and its vegetation are strong enough, orchard heaters will be ignited to protect the citrus crop. At dawn and through the morning hours the smoke from these heaters produces a black pall which hangs over the valley. This aerosol not only appears black in the sky (in contrast to photochemical smog which is usually white) but it appears black when impacted on a target. Such a sample, since it is principally elemental carbon particles, shows no infrared bands. If the minimum temperature is above freezing the heaters will not be used but the radiation inversion is still very strong and will trap vehicle exhaust gases from the morning traffic as well as industrial emissions. High levels of primary pollutants (CO, NO_x, HC etc.) can be measured even though the visibility is unimpaired. This observation was first made by P. L. Haust in December 1956 in South Pasadena (Figure 11).[8] It clearly demonstrates that unreacted auto exhaust (and with lesser certainty other sources) makes little or no contribution to visibility loss. Additional measurements made on similar mornings in Riverside have amply confirmed this conclusion and provided some additional data. One such morning was 10 Feb 1971 when early morning samples were taken on the roof of a five-story office building in central Riverside. The photograph Figure 12 shows unimpaired visibility of the San Gabriel mountains about 21 miles distant. Analyses by gas liquid chromatography, in contrast, show high levels of hydrocarbons in the pattern of auto exhaust emissions (Figure 13). The particle count, included in Figure 10, was about ten times lower than for heavy smog although the hydrocarbon levels were several times larger in this early morning sample. Even this particle count is larger than would have been anticipated from the apparent visibility. Perhaps these observations could be reconciled by suggesting that those particles present in the early morning are black rather than white. Impaction samples taken at this time showed only tiny infrared bands (Figures 14 and 15), but the sample was visible on the BaF_2 target. In fact, photomicrographs showed these particles (Figures 16 and 17).

This observation is dealt with at some length because it has a direct practical application to control strategy: control of primary auto exhaust particulates will not result in any visibility improvement. On the other

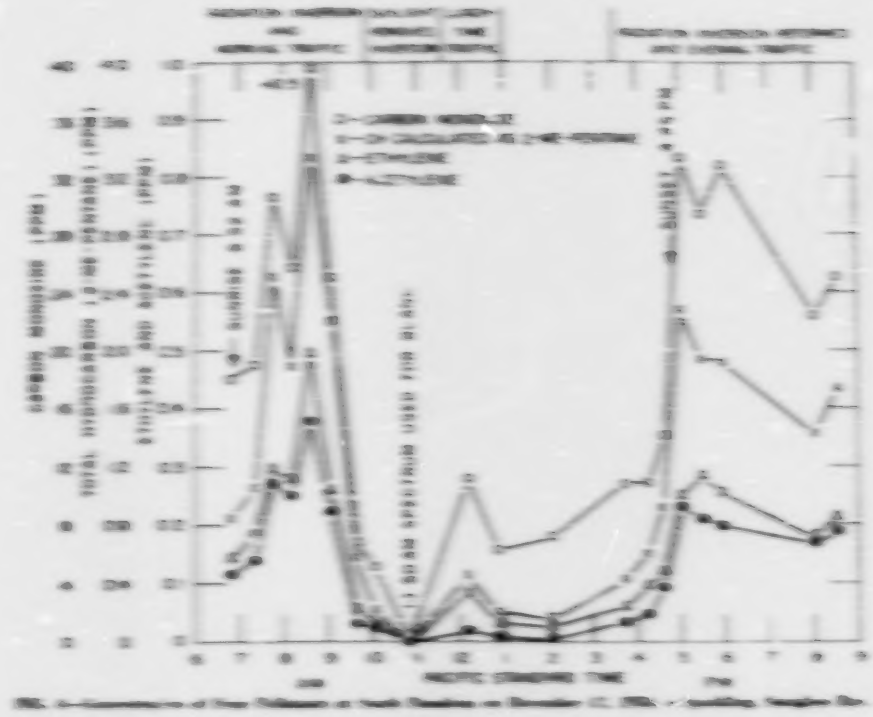


Figure II. Concentrations of pollutants on a smog-free day in 1950 showing accumulation of unphotolyzed pollutants under a radiation inversion. (9)

Figure 12. Clean air at 7:30 AM, 24 February 1972, over central Riverside. See particle count in Figure 10 and hydrocarbon analysis in Figure 11.

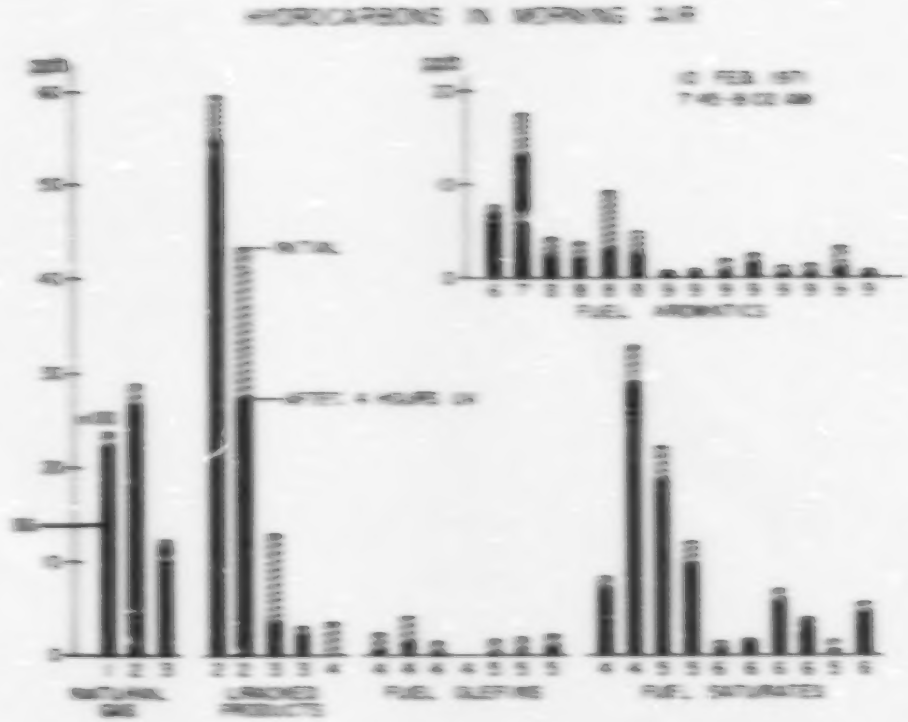


Figure 13. Hydrocarbon analysis in "clean" morning air 10 February 1971 (see Figures 10 and 12; also ref. 11).

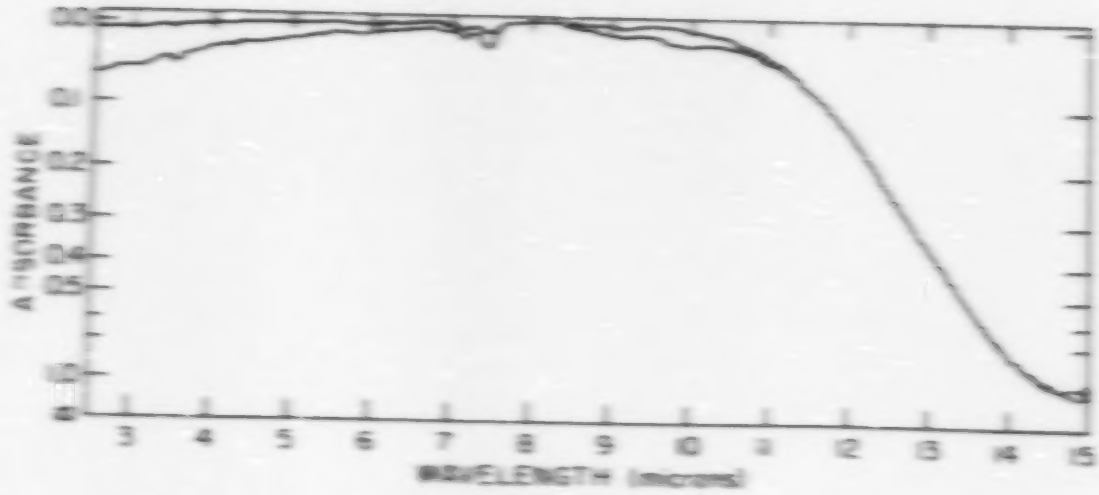


Figure 1A. Infrared spectrum on SnF_2 (large particles; diameter $\geq$ ~1 micrometer) at "clean" working air of 10 February 1971. Note scattering of short wavelengths and weak band at 10 microns.

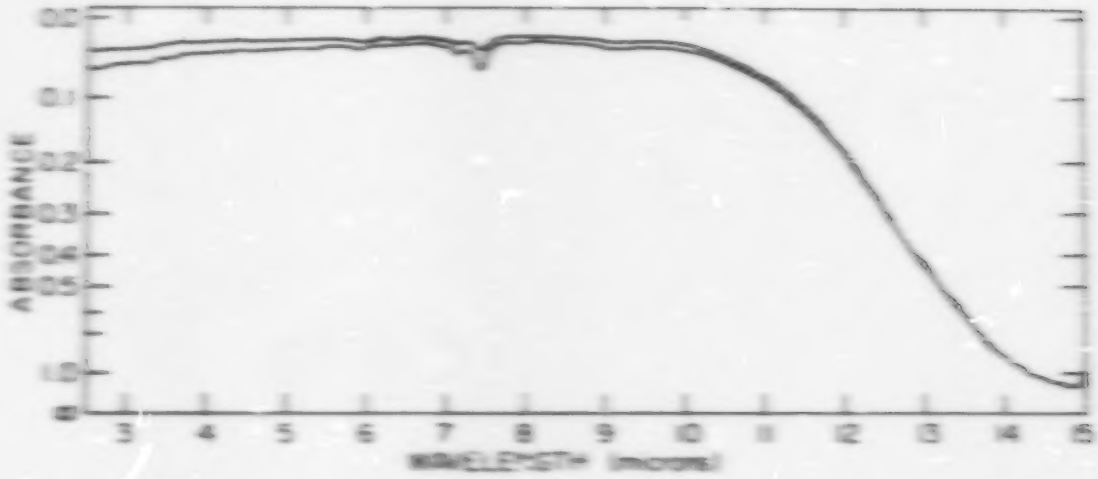


Figure 15. Infrared spectrum on BeF_2 (small particles; diameter ≤ ~1 micrometer) of "Clean" morning air of 10 February 1971. The significance of the bands at 7-7.5 micrometers is unknown.

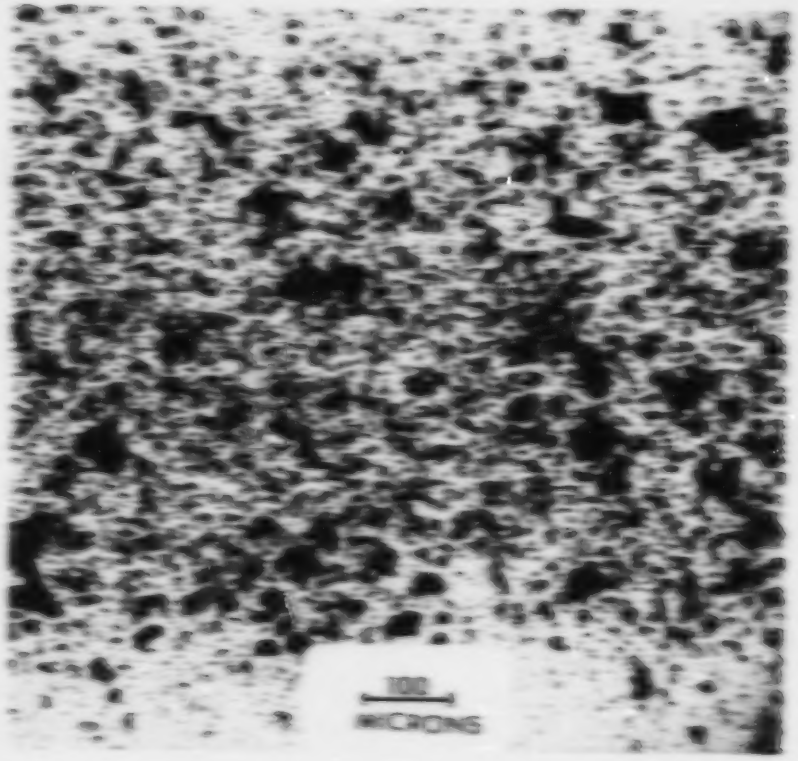


Figure 15. Photomicrograph of large particles shown spectrum is shown in Figure 14. Tan color predominates; looks like sand.

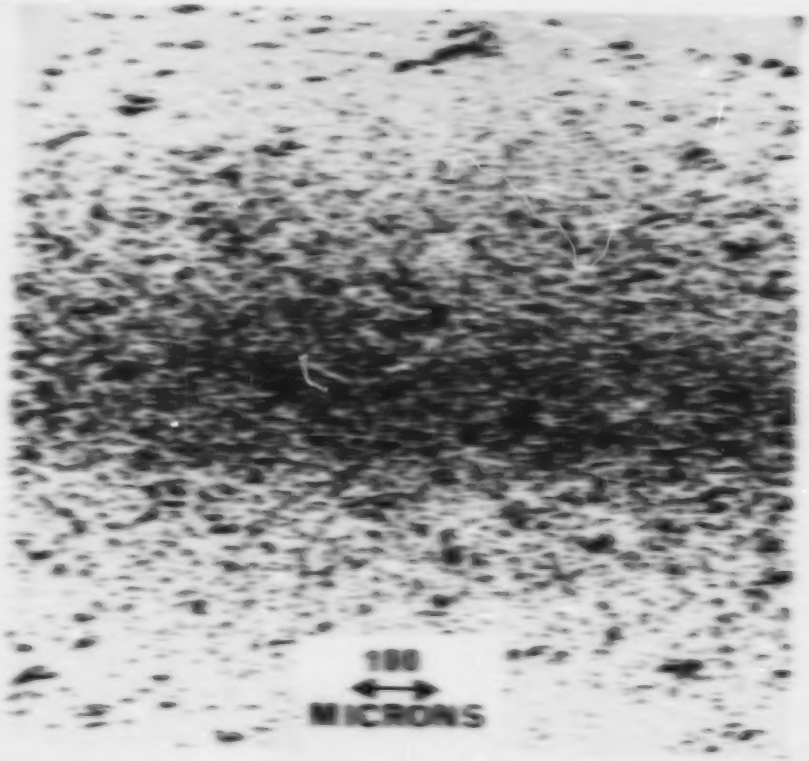


Figure 17. Photomicrograph of small particles whose spectrum is shown in Figure 15. Black particles look like carbon.

hand, secondary pollutants formed by the photolysis of auto exhaust play a vital role in generation of light scattering particulate.

IMPACTOR SAMPLING

The appearance of the photochemical smog samples from the two impaction stages are strikingly different. The first stage (larger particles) supports a golden brown deposit about one mm wide by 15 mm long while the smaller particles on the second stage give jet black lines narrower than the first stage. With moderate magnification the sample of larger particles shows many tan, white and brown angular particles which are obviously solids with irregular shapes. These are considered to be soil dust.

It is evident that windblown soil dust makes an important contribution to total aerosol weight by contributing large particles (diameter greater than 1 or 2 micrometers). The sample of smaller particles shows many black soot-like particles. It is probable that these are in fact carbonaceous particles from combustion sources (autos, trucks, etc.). Both samples when viewed with magnification showed many liquid drops. When exposed to humid air these drops grow and coalesce into a dirty liquid mass.

The model 137 spectrometer is a simple student-type prism instrument with low resolving power. This is no handicap because the aerosol spectra have no fine structure to be resolved. A typical spectrum of smog aerosol obtained with the microspecular reflector is shown in Figure 18 (second stage = small particles). The particle count at sampling time (1015 to 1050) was 12×10^6 ft^{-3}. Heavy haze was present and a strong spectrum (too strong actually) was obtained. The bands are assigned as follows: 3.0-3.5 microns = primarily water (OH stretch) with ammonium ion and some CH possible (3.4 microns); 7.8 microns = ammonium and nitrate ions; 9 microns = sulfate ion; 12 and 14 microns = nitrate ion. The bands at 5 and 6 are ascribed at least in part to liquid water. The carbonyl stretching vibration at 5.75 micrometers would be a useful diagnostic test for organic molecules if it could be clearly identified. It may be noted that the band at that wavelength (5.75) in PAN is due not to a carbonyl but to a peroxy nitrate group.[9][10] More detailed interpretation of these spectra are not easy especially since significant shifts of the band maxima occur depending on sample conditions. If these shifts could be interpreted unambiguously such spectra would be a

much richer source of information. Careful washing of this sample removed most of the spectrum. The resulting spectrum, also shown in Figure 18, shows bands at 4.3 and 5.3 to 7.5 microns which arise from gaseous CO_2 and H_2O in the extra air path of the reflectance attachment. Aside from general attenuation at the shortest wavelength ascribed to scattering no absorption bands survived the water treatment. This experiment, repeated many times, is taken to mean that the bulk of the impacted aerosol is water soluble. Spectra were run at low resolution on a Perkin-Elmer Model 137 (NaCl prism). Through the courtesy of Dr. P. L. Hanst and Mr. Bruce Gay one pair of samples were run on a Fourier Multiplex Spectrometer at EPA laboratories in North Carolina. These spectra (Figures 19 and 20) (taken by transmission through KRS-5) show no fine structure not present in spectra of similar samples taken with the Model 137 (Figures 21 and 22). In fact, the spectra were nearly identical. Figures 23 through 26 show spectra obtained on a day (16 April 1973) of lower aerosol count ($6.5 \times 10^5/ft^3$) with two-hour sample (1645-1845 PST). After running the spectrum with the sample exposed to (ambient) room air it was rerun while exposed to dry air and then a third time while exposed to wet air (Figures 23 and 25). Then the spectra were run once more in ambient air before they were washed with benzene and then with water (Figures 24 and 26). Neither exposure to dry air nor benzene washing caused significant change in the spectra. Exposure to wet air changed the spectrum substantially, enhancing (usually) the bands ascribed to water and changing the shape and sometimes the wavelength of the maxima. A broad band centered near 10 microns in the large particle spectrum survived the wash by both solvents (Figure 24). This substantiates the assignment of this band to silicate mineral dust. None of these spectra showed any sign of a CH band after water washing. It is possible to judge the importance of windblown dust and carbonaceous particles by sampling when these conditions predominate. Santa Ana wind conditions provide atmospheric dust although the loss of visibility and the aerosol count are not as large as one would imagine (see Figure 10). When orchard heaters are used on cold nights carbonaceous aerosols accumulate to form a visible but black aerosol. Neither of these aerosols show any infrared bands when impacted.

It was previously reported that the aerosol present in unreacted but contaminated air had about one tenth the particle count of photochemical

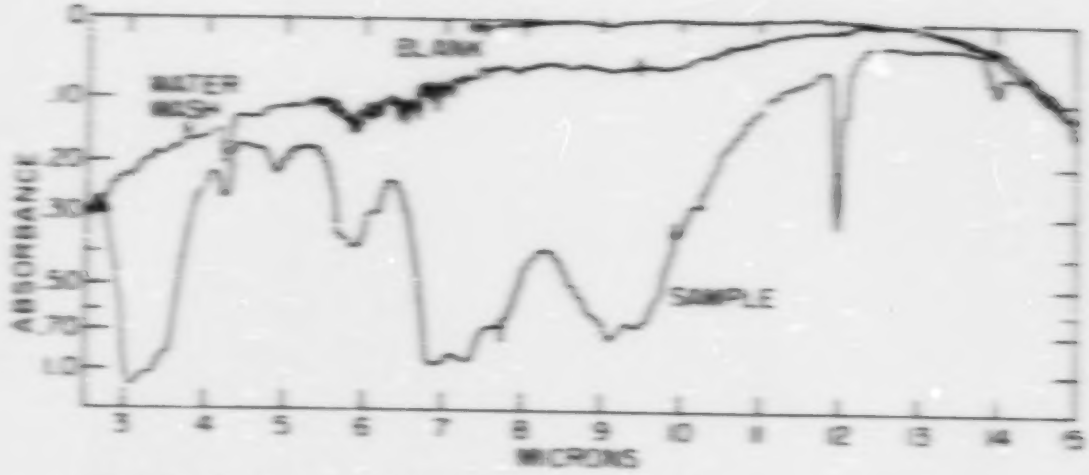


Figure 18. Typical smog aerosol reflectance spectrum. Band assignments in the text. Water washing removed all bands except air path water and CO_2 and scattering at short wavelength.

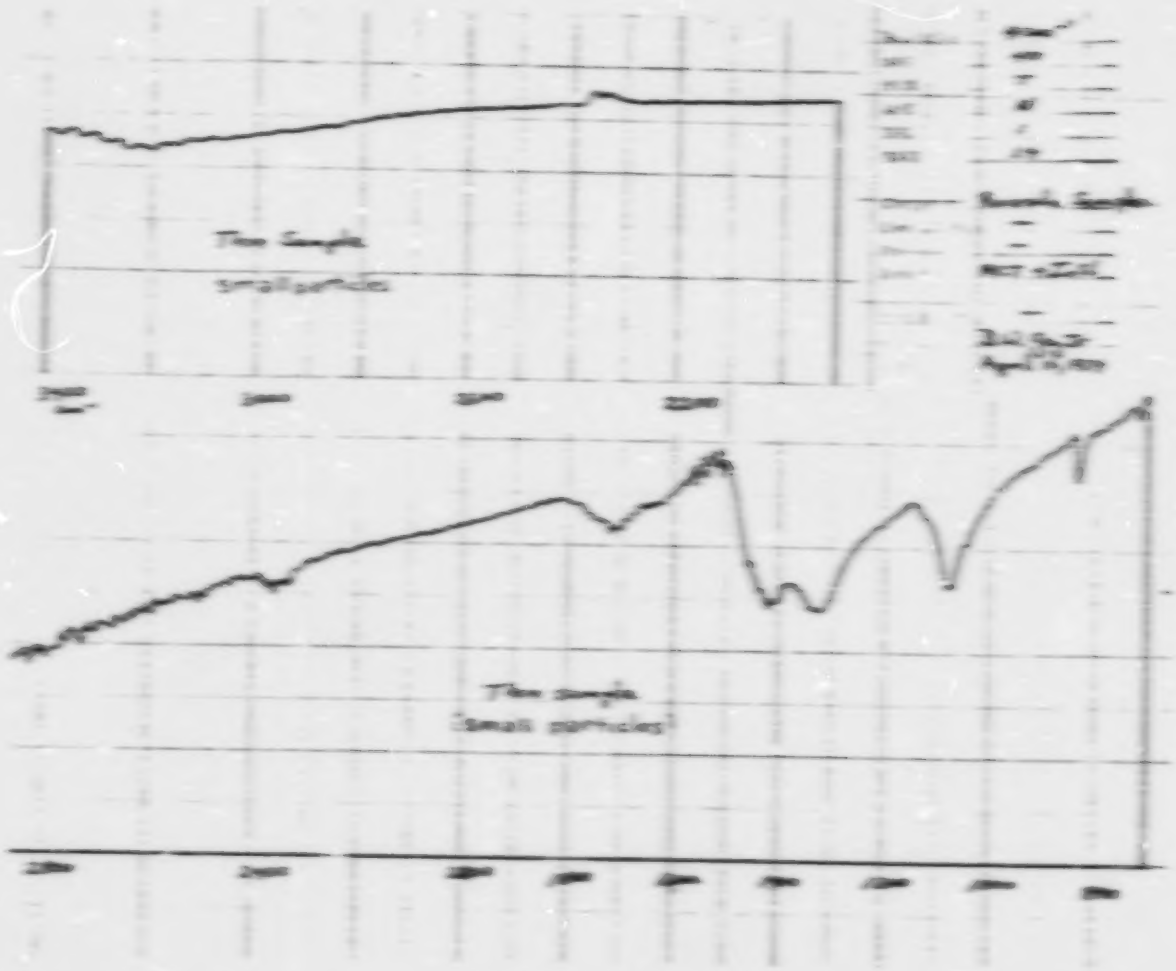


Figure 19. Fourier transform spectrum of Riverside aerosol small particles on KBS-5 (transmission)(run at EPA Laboratories by R. W. Gay, Jr.). Compare small particle spectrum with Figure 21.

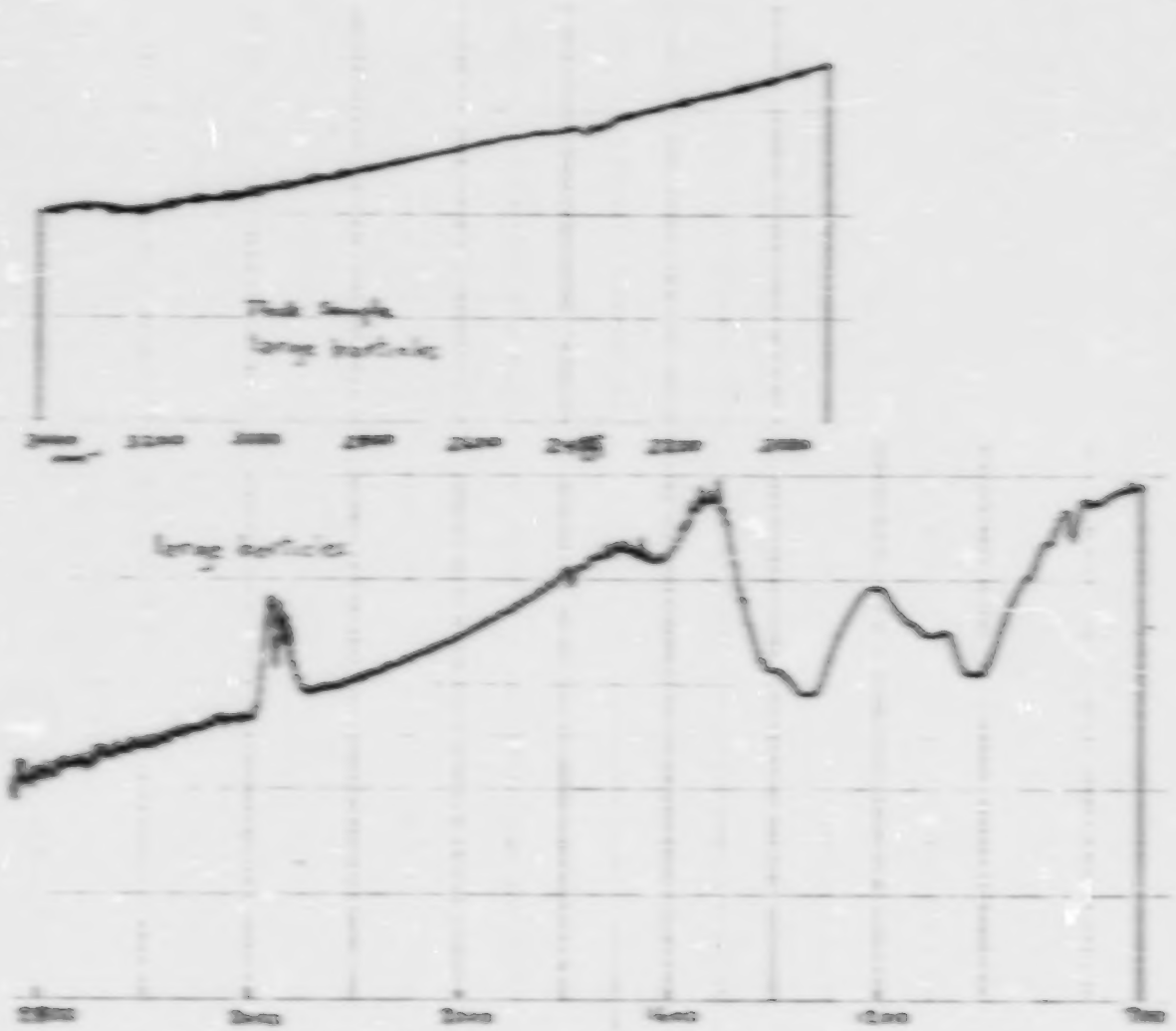


Figure 23. Fourier transform spectrum of Riverside aerosol large particles on ERS-5 (transmission)(run at EPA laboratories by R. W. Gay, Jr.). Compare large particle spectrum with Figure 22.

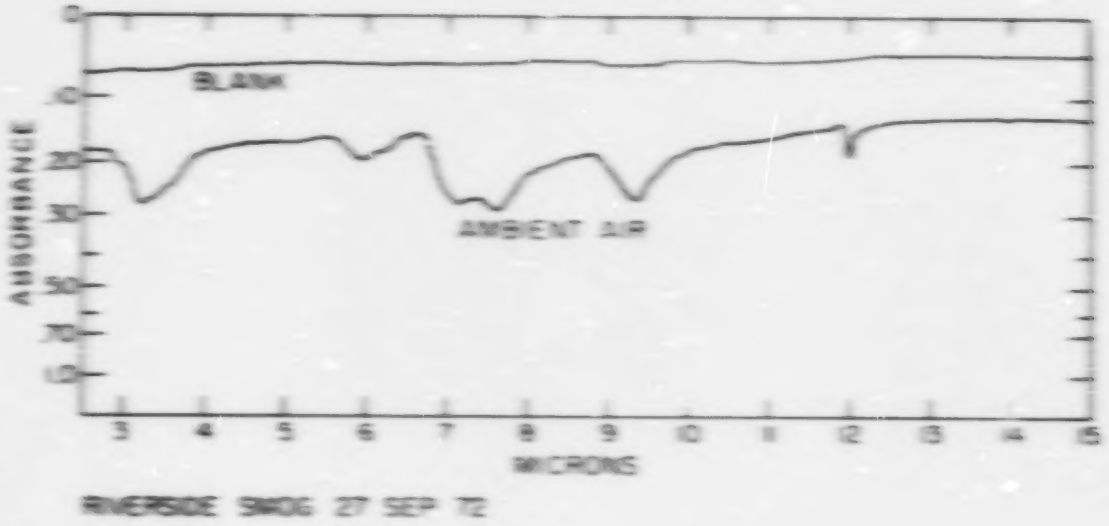


Figure 21. Prism spectrum of ambient aerosol (small particles) on KBr-1 shows the same bands as the FTS spectrum of Figure 19.

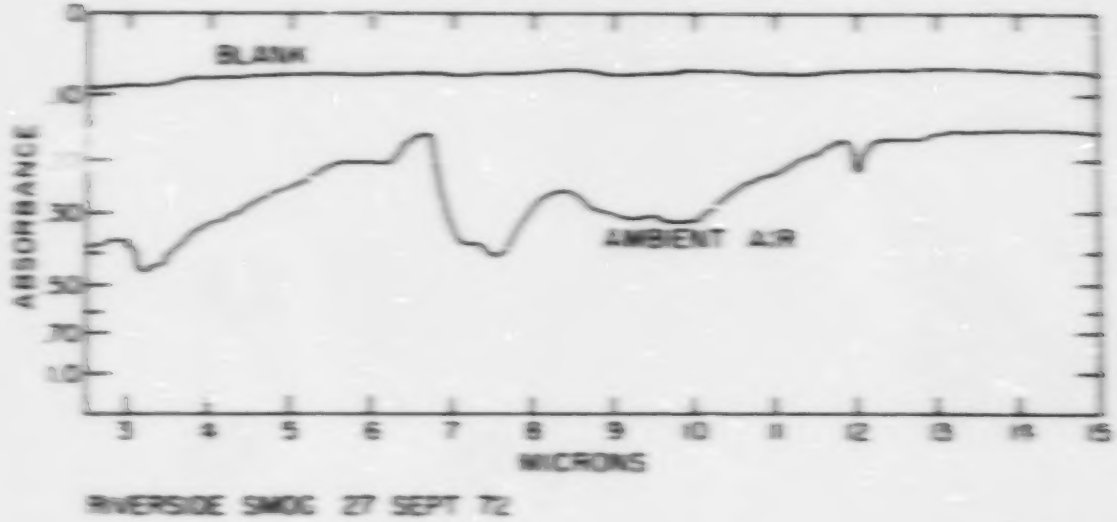


Figure 22. Prism spectrum of ambient aerosol (large particles) impacted on KRS-5 shows the same bands as the FTS spectrum of Figure 20.

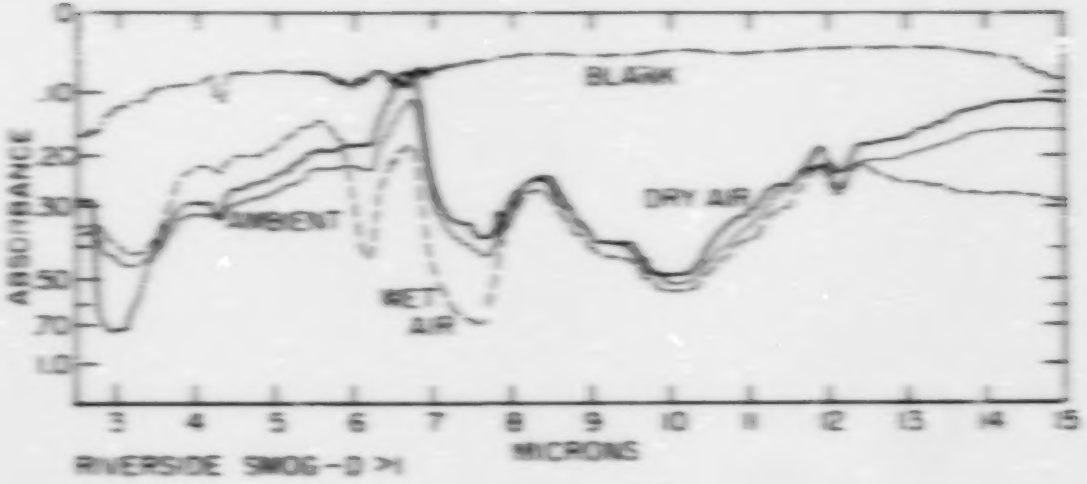


Figure 11. Ambient aerosol large particles (in April 1973) showing enhancement of some bands in response to moist air exposure. No effect of dry air.

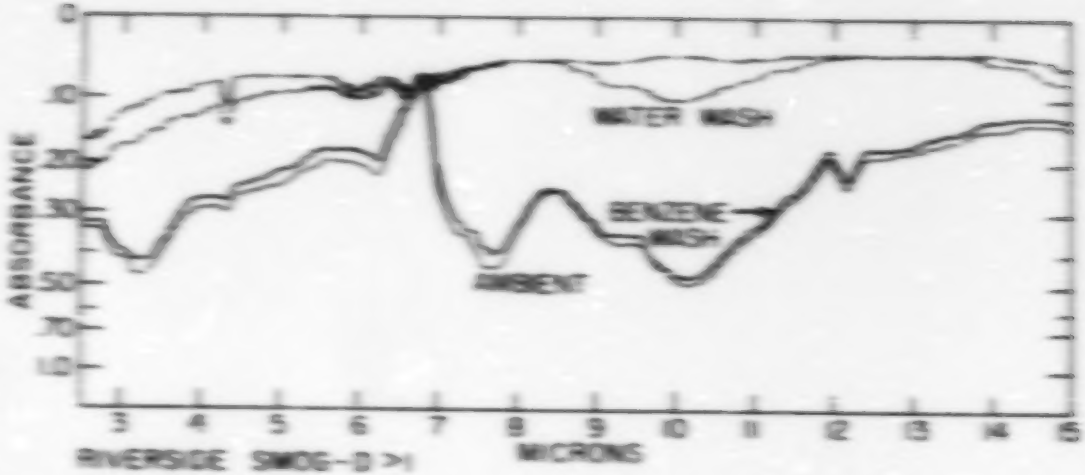


Figure 24. Washing of large particle sample of Figure 23 with benzene did not change the spectrum significantly. Washing with water removed all but the broad 10 micrometer band attributed to silicate.

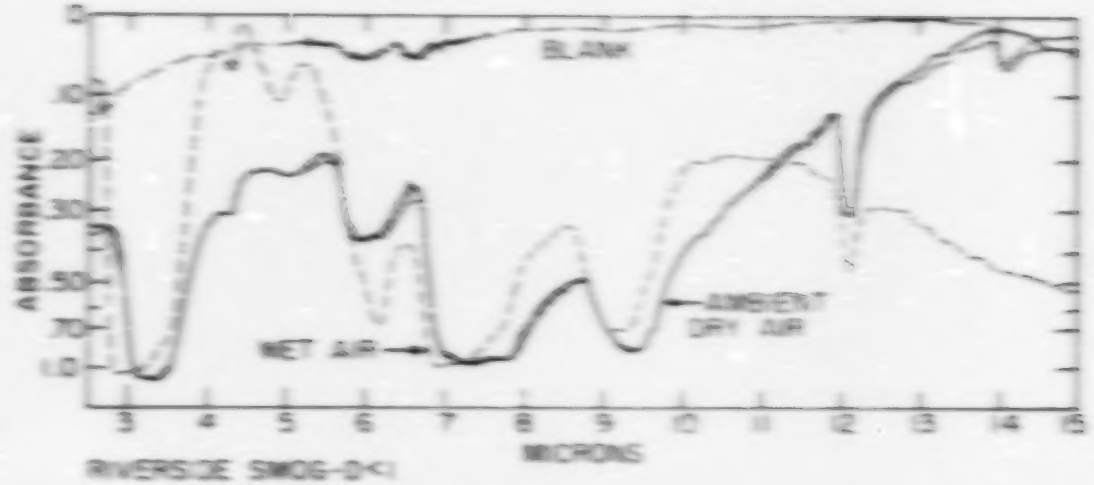


Figure 15. Ambient aerosol small particles (24 April 1973) showing enhancement of water bands in moist air exposure. No effect of dry air.

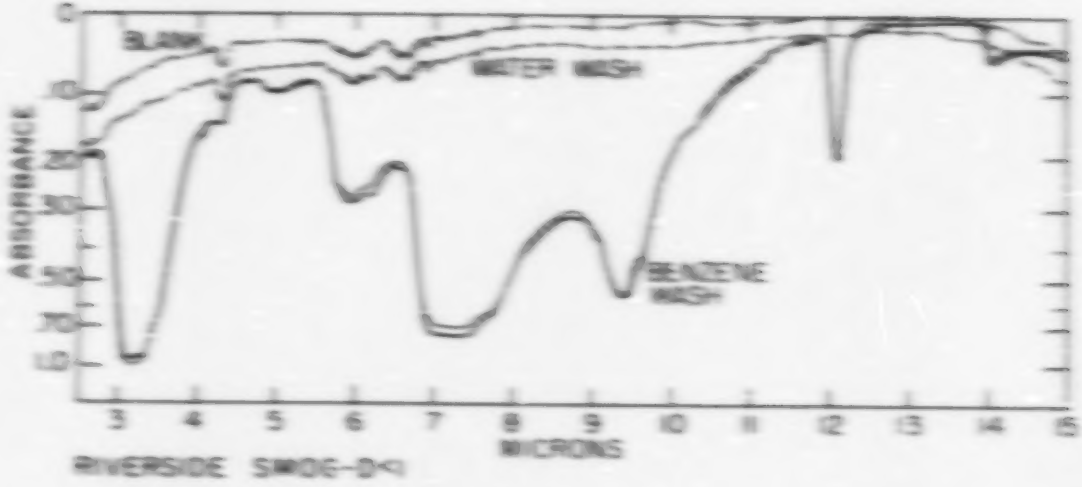


Figure 26. Washing of the small particle sample of Figure 25 with benzene had no effect on the spectrum, but water washing removed the sample completely.

smog even though there is no apparent degradation of visibility. The early morning hours of the 25th of January 1974 presented an opportunity to obtain spectra of such aerosols. A pair of samples were taken from 7:30 to 9:30 PST in Central Riverside after a good atmospheric purge. Chromatographic hydrocarbon analyses indicated high concentrations of unreacted auto exhaust; the acetylene increased from 35.6 to 71.8 ppb during the sampling interval. Visibility remained excellent and b_{scat} values of 8.5×10^{-5} m^{-1} were observed in the area. Surprisingly the visual appearance of the samples was similar to that of photochemical smog samples; the larger particles had a tan color while the small particles appeared black. The black sample (small particles) showed no infrared bands (Figure 27) while the large particles showed a broad band at ten microns which is ascribed to silicate minerals (Figure 28). These observations indicate that these primary aerosols do not contribute substantially to visibility loss.

The assignments of these bands are based on reference spectra, one set of which was obtained by pressing water solutions of inorganic salts between KRS-5 windows. The bands of liquid water are so strong that no spacer could be used. Therefore the spectra cannot be used quantitatively. Water (Figure 29) shows strong bands at 3.0 and 6.1 micrometers, analogous to the bands of water vapor. There is a weaker band at 4.8 micrometers. Sodium sulfate solution (Figure 30) showed, in addition to these water bands, a strong band at 9.1 micrometers. Many ambient air spectra show a strong band near this wavelength. Sodium nitrate solution (Figure 31) shows a strong band at 7.3-7.3 microns assigned to the nitrate ion. The weak band at 12 micrometers apparently coincides with the distinctive sharp band at this wavelength in ambient aerosol spectra. The difference in sharpness is ascribed to the liquid water environment. The absence from Figure 31 of the weak band at 14 micrometers which is ascribed to nitrate in the ambient aerosol spectra is also attributed to this environment. Ammonium chloride solution (Figure 32) shows a strong band at 7 micrometers and the water band at 3 microns is broadened on the long wavelength side. This is, of course, the NH stretching

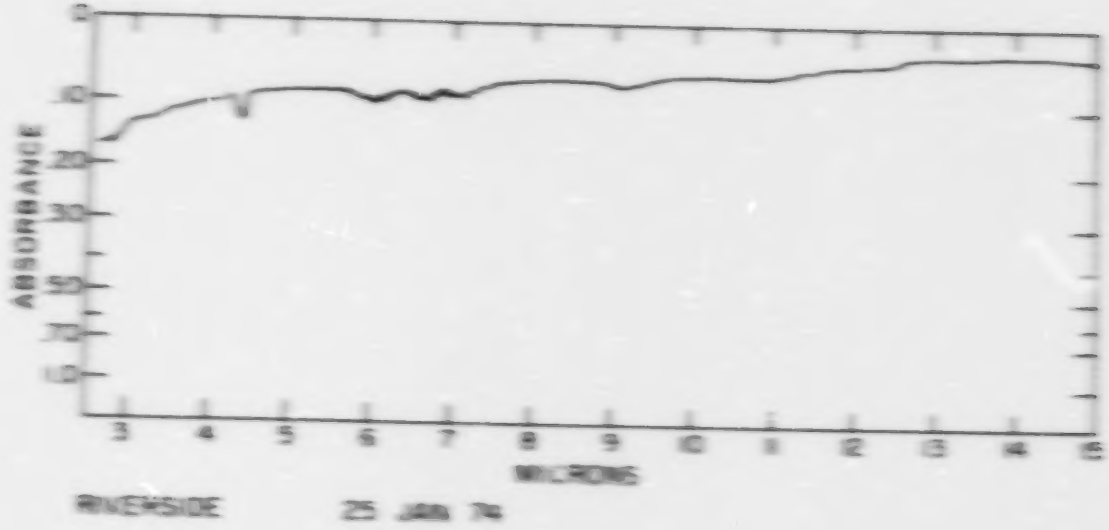


Figure 17. Impaction of morning air: small particles. No absorption bands are seen even though a black sample was visible.

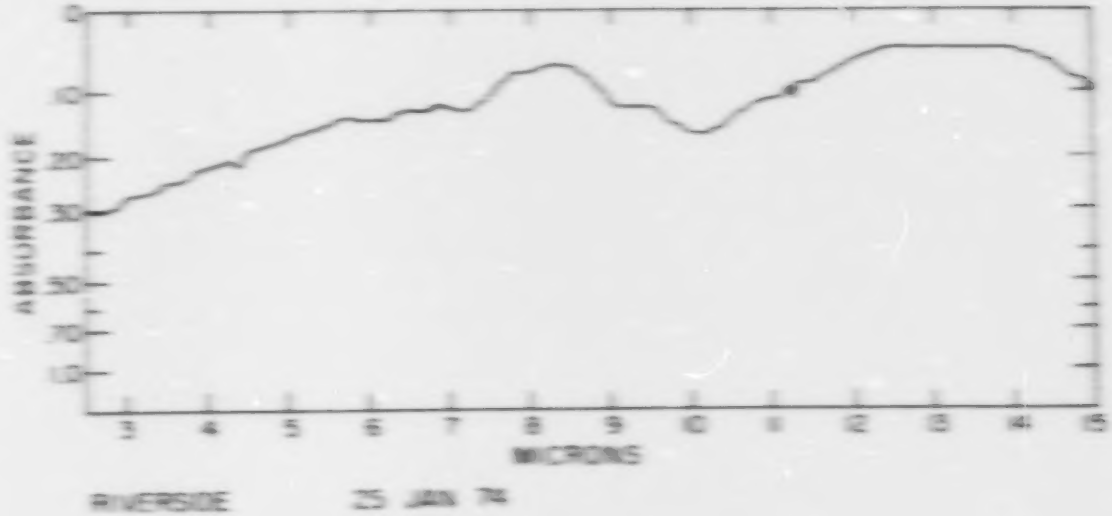


Figure 28. Impaction of morning air large particles. Only the broad "dust" band at 10 micrometers is visible. Usually the sample was light brown.

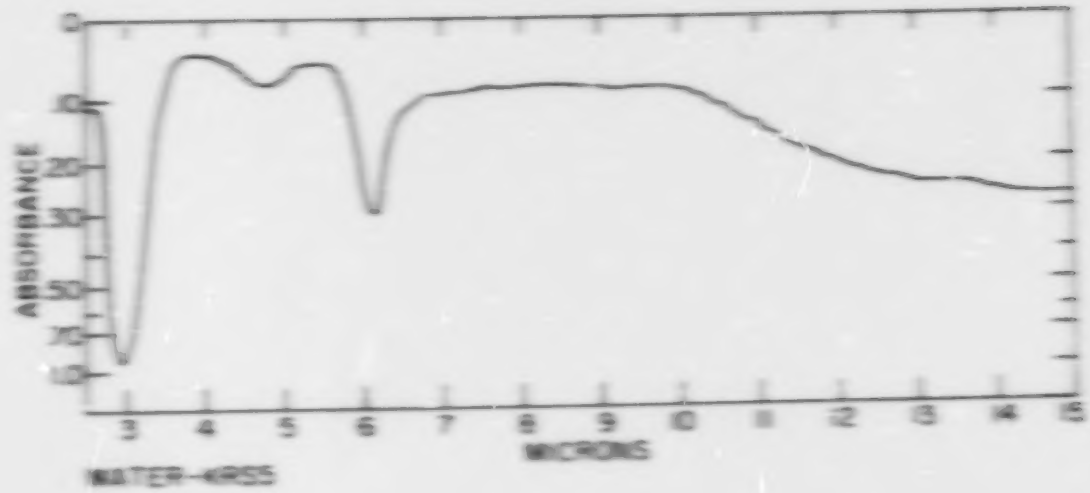


Figure 29. Infrared spectrum of liquid water in a thin film between NBS-1 plates.

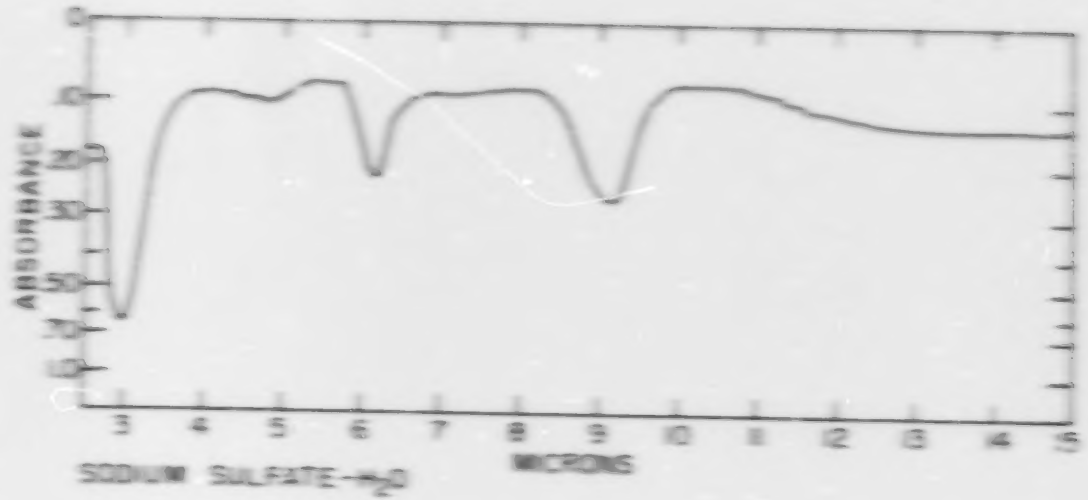


Figure 30. Infrared spectrum of aqueous sodium sulfate between 110-5 places.

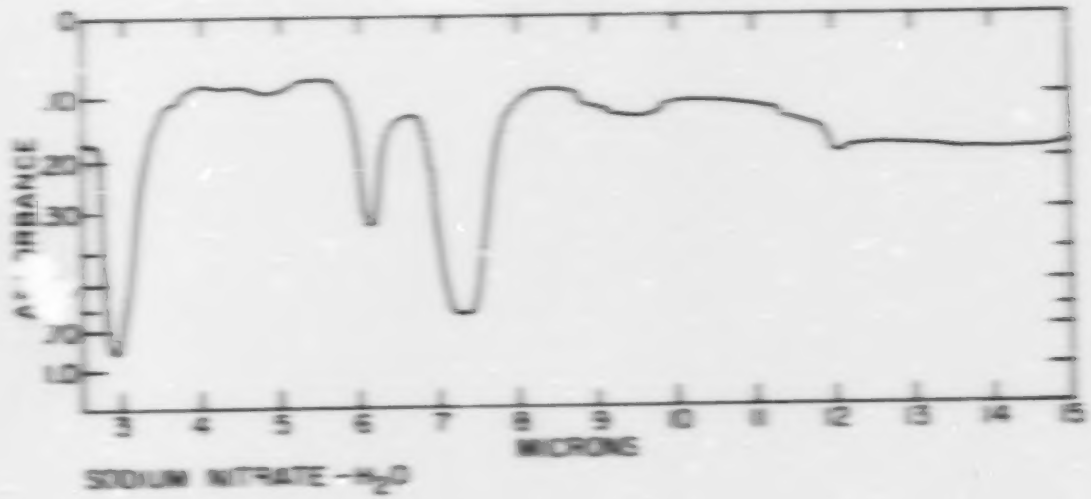


Figure 31. Infrared spectrum of aqueous sodium nitrate between 625-5 places.

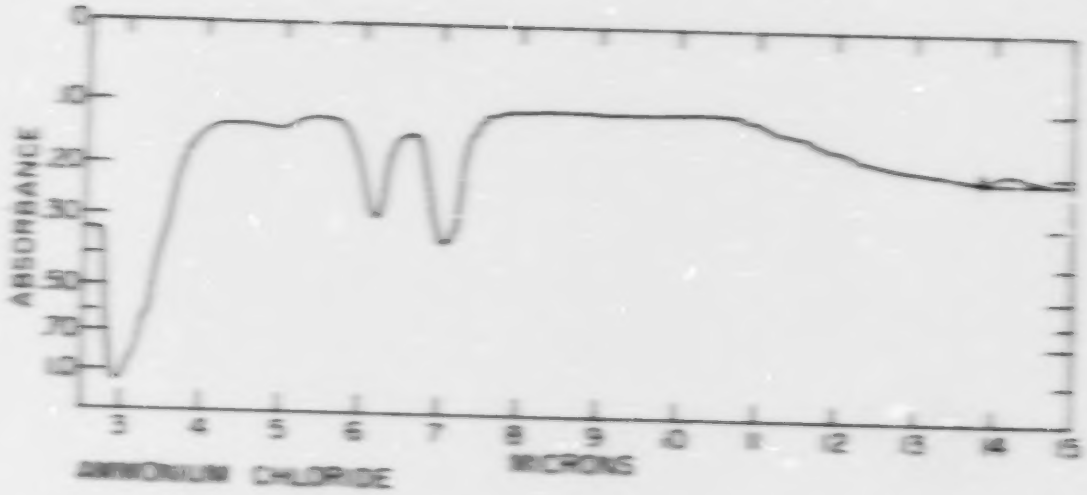


Figure 11. Infrared spectrum of aqueous ammonium chloride between KBr-I plates.

vibration.

Spectra of the combination salts, ammonium sulfate and ammonium nitrate, and various salt mixtures were also run and found to be consistent with superposition of the simpler spectra. There is, however, evidence that spectra are dependent on water content. Most striking is the behavior of the nitrate bands; when a nitrate salt is dried, the bands at 9.7, 12.15, and 14.1 micrometers become much stronger and sharper. Synthetic aerosols were generated from the sulfuric and nitric acids mixed with ammonia, and impacted onto a reflectance plate (Figure 11). The three nitrate bands are sharp in this spectrum. The sulfate band is unchanged in wavelength while the ammonium band at 7.0 merges with the nitrate band at 7.35 micrometers. This spectrum shows a quite close match with the typical ambient air sample of the smaller diameter particles (see Figure 26 for example).

It was also possible to record spectra of sulfuric acid alone by impacting a synthetic acid aerosol onto a metal target. For this spectrum (Figure 14) the strong sulfate band at 9.15 is replaced by three broad humps at 8.9, 10.0, and 11.7 micrometers. A few spectra, taken at UCLA, showed bands very similar (but not at exactly the same wavelengths) to these (Figures 15 and 16). The nitrate bands are absent from these two UCLA spectra. The reason for the presence of the free acid (apparently) only in these samples is not known. This must represent one of the very few techniques for detection of free sulfuric acid aerosol. Washing with water revealed the typical broad "dust" band at 10 micrometers, particularly in Figure 15. This could account for some of the wavelength shift. Returning to the sulfuric acid reference spectrum, (Figure 14), traces 2 and 3 show the spectrum after exposure of the sample to ammonia gas. The three broad bands are replaced by a single band at 9.6 micrometers which is shifted to slightly longer wavelengths than in Figure 11. The ammonium band is also shifted to slightly longer wavelengths.

Most spectra, and scores have now been recorded using the microreflector technique, show a sulfate band resembling the salt rather than the free acid.

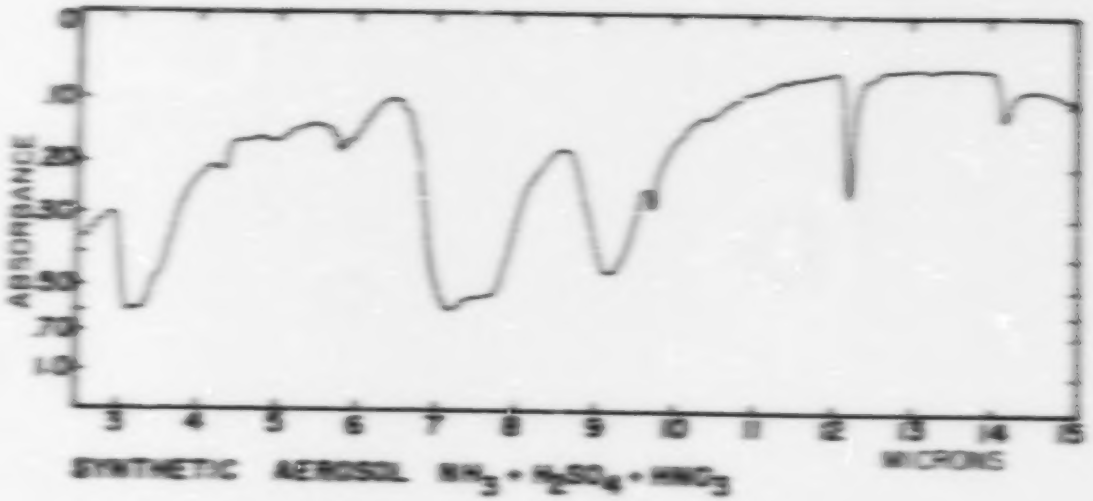


Figure 33. Impacted aerosol synthesized from ammonia with sulfuric and nitric acids. Note the close resemblance to the ambient spectrum of Figures 25 and 26.

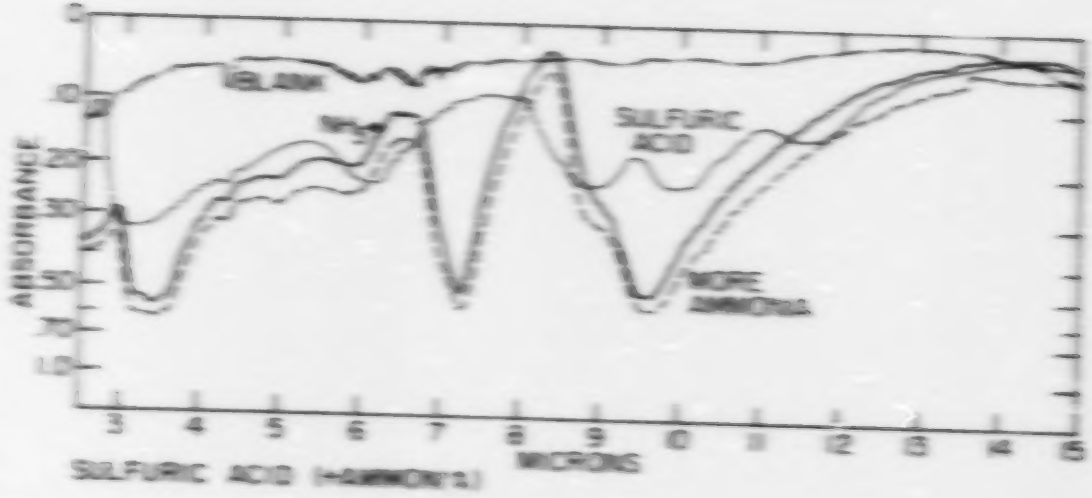


Figure 3a. Impacted sulfuric acid aerosol. Note three broad bands between 8-12 micrometers.

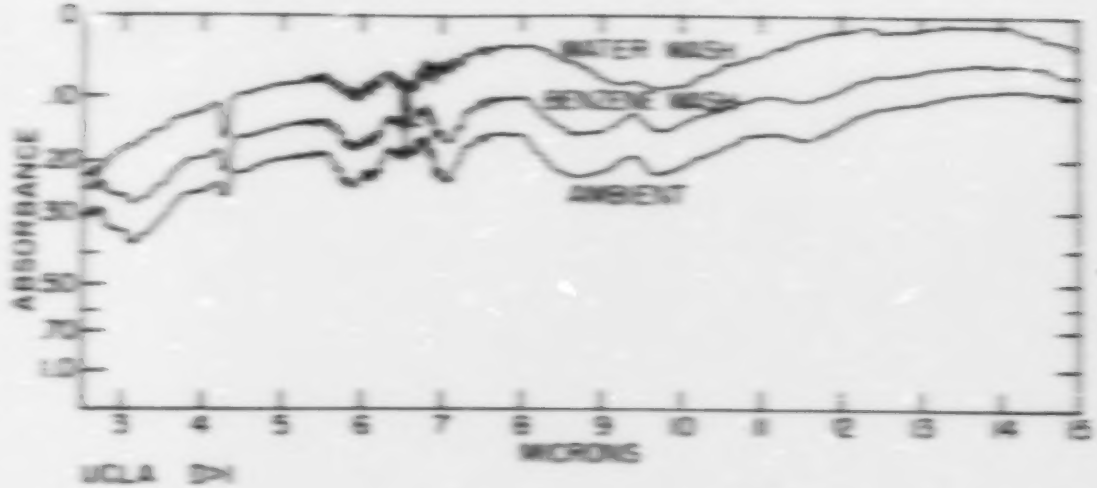


Figure 35. Sample taken on UCLA campus. Note similarity to sulfuric acid sample. These large particles show the dust band after water wash.

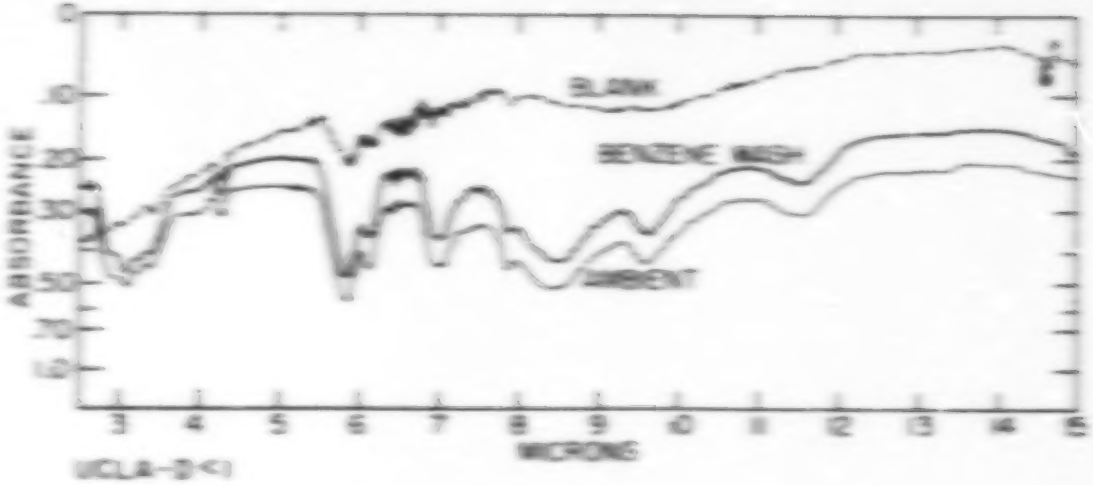


Figure 36. Sample taken on UCLA campus. This slide shows the bands tentatively identified as sulfuric acid.

SOUTHERN CALIFORNIA SURVEY

Ambient air samples were taken during a full day (about 6 A.M. to midnight) on a two-hour cycle at a number of locations around Southern California. This produced well over 100 spectra, which are not easy to summarize since all the nuances of the spectra cannot at this time be interpreted. Since each location was sampled on only one or two days, these cannot be regarded as representative of the various sites. While many spectra were similar to those obtained at UCR, there were definite differences. The following list gives the site and a brief commentary on each group of spectra.

Westwood UCLA - 26 June 1973; 28 June 1973. Bands like sulfuric acid. No evidence of nitrate.

Irvine UCI - 14 August 1973; 16 August 1973. Large particles: dust band. Small particles: weak spectra.

Orange Co. APCD - 12 September 1973; 13 September 1973. Strong spectra. Large particles: dust bands, nitrate bands.

Corrinne - 25 September 1973; 27 September 1973. Strong spectra on 25th; weak on 27th. Spectra on 25th similar to Riverside.

Pasadena Cal Tech - 17 July 1973; 19 July 1973. Strong dust bands, nitrate bands, sulfuric acid, small CH band.

Claremont - 10 July 1973; 12 July 1973. Strong spectra, similar to Riverside.

Green River (Santa Ana Canyon) - 19, 21 September 1973. Unusual spectra, some without nitrate, some like sulfuric acid.

Palm Springs - 7, 9 August 1973. Mostly weak spectra; one clean nitrate, sulfate spectrum.

Rim of the World (San Bernardino Mountains) - 24, 26 July 1973. Weak spectra: sulfate bands.

Only a very few of the samples showed any indication of a CH band indicative of organic material. To verify that the procedures used would show such a CH band if such an aerosol were present, synthetic ozone-olefin aerosol was generated and mixed with the ambient aerosol. A stream of 1000 ppm ozone at 100 ml/min was mixed with 50 ml/min of 3-ethyl-2-methyl-2-pentene in the vapor phase to generate an aerosol which was mixed with ambient aerosol; then

impacted and analyzed in the standard way. The spectra before water wash (Figure 17) resembled the usual ambient air sample with no distinguishable OH band. After water washing a distinct OH band as well as a variety of longer wavelength bands appeared. This the method is capable of revealing organic aerosol when there is enough present. This may be compared with the spectrum of ambient aerosol taken on a day of very heavy haze with 12 million particles per cubic foot; about as high a count as ever seen in Riverside (Figure 18). This strong spectrum, which included distinctive nitrate bands at 12 and 14 micrometers, was completely washed away by water. The strong water vapor bands at 2.7 and 5.3 to 7.7 micrometers in the blank reflect the high humidity of the ambient air that day.

EXTRACTION OF ORGANIC MATERIALS

Although the impaction spectra did not, in most cases, show evidence of organic matter, it is evident that some organic matter is present nevertheless. To obtain spectra of the organic material, aerosol samples were taken on high volume filters which were then extracted with various solvents. To establish a relationship with pollution sources, reference samples were taken of exhaust gases from various engines. These were treated with the same solvents as the ambient air samples to obtain infrared spectra.

Equipment

The ambient air aerosol was collected with a Staples SH810 hi-vol sampler using a 8" Gelman-type A glass filter with a flow rate of 35 CFM. The following modifications were made for the collections of auto exhaust samples: A cone was attached to the hi-vol sampler with the point attached to a "T" made of pvc tubing. One of the ports of "T" was connected to the exhaust tail pipe. The third port was used as a by-pass.

Impaction samples of auto exhaust were taken by connecting the impactor to a pvc "s". The second port was connected to the auto exhaust tail pipe. The third port was connected to a cylinder of compressed nitrogen. The nitrogen was used to cool the exhaust gases and prevent the melting of the impactor wax seal and prevent water from condensing on the impaction plate. The fourth port was used as a by-pass. The samples were collected on KBr-5 plates and scanned by the usual procedure.

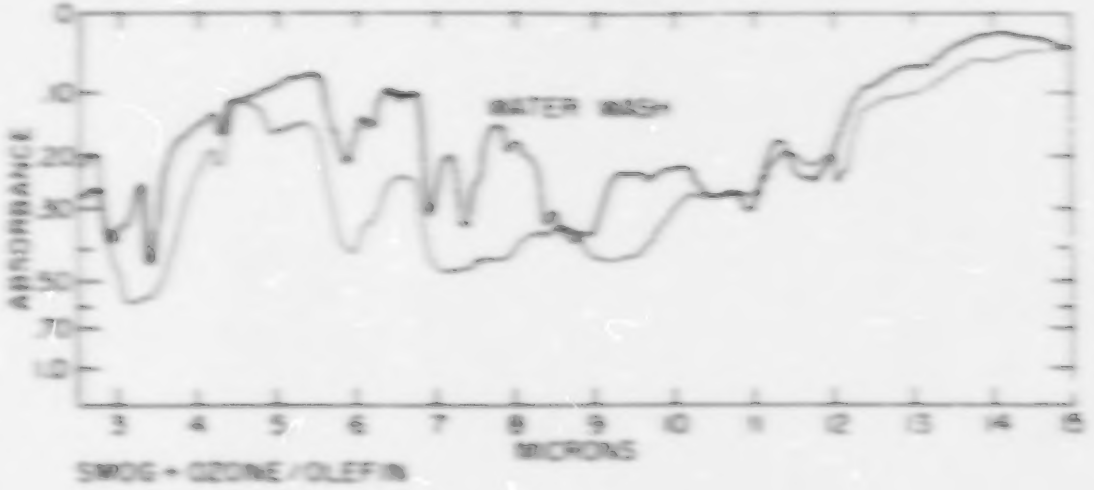


Figure 37. Sample of ambient aerosol mixed with high concentration ozone/olefin reaction products. Water washing removed the neutral aerosol to leave a clear CH and carbonyl band.

Techniques

The hi-vol filter papers were extracted by placing ½ of a filter paper into the soxhlet. 100 ml of solvent were placed in ½ liter flask and refluxed for two hours. The solvent was then distilled off with the last few mls being saved. The solution was taken up in an eye dropper and smeared onto a KRS-5 plate. After the solvent evaporated, the sample was scanned on the IR. The sample was first scanned in an environment of 100% humidity air, and then dry air (0 % humidity). Additional scans were run in an environment of ambient air. First the sample was scanned, then washed with benzene, scanned again and washed with water and then scanned again. The blank was prepared by polishing the plate with tin oxide and methanol on a soft cloth.

Sampling

Twenty-minute hi-vol samples were taken from the exhaust of a 1970 gasoline powered Chevrolet pick-up (UCR vehicle 5-830). The truck was standing and running at idle speed. The filter papers were cut in half and extracted. A ten-minute impaction sample was collected.

Ten-minute hi-vol samples were taken from the exhaust of a 1960 Ford 5000 diesel tractor. The tractor was standing and running at idling speed. The filter papers were cut in two and extracted. A five-minute impaction sample was selected.

Twenty-minute hi-vol samples were taken up from the exhaust of a propane powered pick-up (UCR vehicle 5-828). The truck was standing and running at idle speed. The filters were cut in two and extracted. A 30-minute impaction sample was collected.

These spectra are summarized in Table 5.

The polar solvents (water, methanol, acetone) produced spectra of ambient aerosols similar to direct impaction with only marginal evidence for organic molecules. The nonpolar solvents showed distinctive CH bands and bands in the carbonyl stretch region. The various engine exhaust samples resembled the ambient air spectra in a general way, but the agreement was far from complete. Methods like these hold promise for distinguishing organic matter emitted directly from engines, from that formed photochemically in the atmosphere.

TABLE 4. INFRARED BANDS (MICROMETERS) OF AMBIENT AND EXHAUST AEROSOLS

CH_2Cl_2 extraction									
Ambient air	3.0	3.5	5.9	6.2	7.0	7.6	7.9	8.0-10.0	11.7
Gasoline exhaust	3.0	3.5	5.9	6.2	7.0	7.6	7.9	8.0-10.0	
Diesel exhaust	3.0	3.5	5.9	6.2		7.6	8.0	8.0-10.0	
Propane exhaust		3.5	5.9	6.2		7.6	7.9		
						7.6	7.9		
CH_3COCH_3 extraction									
Ambient air	3.3	5.9	6.2	7.3	7.6	8.3	8.7	9.6-10.6	12.1
Gasoline exhaust	3.4	5.9	6.2	7.3					
Diesel exhaust	3.4	5.9							
Propane exhaust	3.4	5.9							
$CH_3CH_2OCH_2CH_3$ extraction									
Ambient air	3.0	3.4	5.9	6.2	6.9	7.3	7.6		11.7
Gasoline exhaust	3.0	3.4	5.9		6.9	7.4			
Diesel exhaust		3.4	5.9	6.2	6.9	7.3			
CH_3OH extraction									
Ambient air	2.8	3.4	5.1	5.8-6.3	6.8	7.4	9.6	12.0	
Gasoline exhaust	3.0	3.4	5.8	6.3	6.8	7.4	9.6		
Diesel exhaust		3.4	5.8		6.8				
Propane exhaust	3.0	3.4	5.8	6.3	6.8	7.4	9.6	12.0	
C_6H_6 extraction									
Ambient air	3.0	3.4	5.8	6.2	6.9	7.4	7.9	9.0-10.0	11.7
Gasoline exhaust		3.4	5.8		6.9			9.0-10.0	
Diesel exhaust	3.0	3.4	5.8	6.2	6.9	7.4			
H_2O extraction									
Ambient air	3.0			6.2			8.0-10.0		
Gasoline exhaust	3.0			6.3			8.0-10.0		
Propane exhaust	3.0			6.3			8.0-10.0		
1.1 mm slit impaction									
Ambient air	3.0 - 3.2			6.2	7.0-8.0				
Gasoline exhaust					7.0				12.3
0.38 mm slit impaction									
Ambient air	3.0-3.2		5.9	6.2	7.1	7.6	9.3		
Gasoline exhaust			5.8	6.3			9.6		12.0
Diesel exhaust	3.3								12.0

In addition to these spectral studies, some carbon/hydrogen analyses have been obtained by the classical combustion technique. For this analysis glass fiber filter samples were obtained over a 96-hour period from May 11-15, 1973. Each of six filter strips was weighed before and after sampling and again after soxhlet extraction with one of five solvents. The extracts were reduced in volume by evaporation and 15 ml of 50 ml concentrate was evaporated onto an infrared window to obtain an infrared spectrum. The remaining 35 ml of extract were evaporated on pre-weighed glass fiber filters. After all the solvent had evaporated, reweighing gave the weight of soluble material deposited on the filter. These were then sent out for combustion analysis. A blank was run on the filter paper. Table 5 gives data for these experiments. The principal conclusion is that the proportion of organic

TABLE 5. CARBON/HYDROGEN ANALYSIS OF AMBIENT AEROSOL EXTRACTS

Solvent	Weight[a]	Wt. loss extraction		Extract		% of total sample	
	mg	mg	%	%C	%H	%C	%H
Ether	198	41	20.6	13.6	7.9	2.8	1.6
CH_2Cl_2	130	33	25.4	12.9	6.6	3.3	1.1
C_6H_6	134	24	17.9	23.4	4.4	4.2	0.8
Acetone	70	64	91.4	0.5	0.5	0.3	0.3
MeOH	159	105	67.7	2.1	2.1	1.5	1.4

[a] In approximately 960 m^3 of air sample

carbon is quite small. The hydrogen analysis is much more uncertain since there was no way to insure that all the water had been removed from the paper prior to analysis. The C/H atom ratios are not very consistent or easily interpreted in terms of organic structures. Since visual examination of the aerosols always shows black particles which are probably mostly elemental carbon, an attempt was made to extract all the organic carbon by extracting a filter, first with ether, then with methylene dichloride, then with benzene and finally with methanol. These samples contained 22.5% carbon and 6%

hydrogen before extraction and 26.7% carbon and 5.9% hydrogen after extraction. Another 24-hour hi-vol sample contained 11.4% carbon and 7.4% hydrogen. These analyses are consistent with the view that there is considerable elemental carbon in the ambient aerosol.

PHOTOCHEMICAL FORMATION OF AEROSOLS

A complete account of photochemical aerosol formation would include a demonstration that realistic aerosol concentrations can be formed from realistic concentrations of reactants. This has not been clearly demonstrated for any of the known aerosol-forming mechanisms. Several laboratories have shown aerosol formation at high (ppm) concentrations of olefins irradiated with nitrogen oxides. In our earlier work spectra of such aerosols were obtained which showed clear CH bands.[1] To extend this work to lower concentrations a series of experiments were done with the flow tube photoreactor using α-pinene and NO_2 as reactants. Concentrations down to 1/32 ppm (31 ppb) of α-pinene were used with residence times up to eight hours and a 2/1 ratio (by moles) of the hydrocarbon to NO_2. The aerosol was counted with the Bausch and Lomb 40-ia dust counter for particles larger than 0.3 micrometer in diameter.

Compressed air from the house supply was purified with a heatless "dryer" in which charcoal was used in place of the desicant. After leaving the purifier this air was humidified by passage through an ice bath. It was found necessary to pass the air through a 0.3 micrometer filter to obtain a zero background count on the air entering the reactor. It was also important to prevent back flow and diffusion of room air into the reactor outlet. Counts made under these conditions showed no countable particles entering the reactor from the input manifold and showed the same reading at the reactor exit (dark). The reactants were dispensed into the airstream from 15-liter low pressure breathing oxygen tanks. Although the reactants were made up by well established procedures, that is adding liquid to a "low pressure oxygen" (LPO) tank and pressurizing it with nitrogen, and the input concentrations are calculated by the ratio of input reactant stream to input airstream, no actual measurements of the reactants were made and therefore there is some uncertainty as to accuracy of the concentrations. The results are summarized

in table 6.

TABLE 6. AEROSOL PRODUCED BY THE PHOTOCHEMICAL REACTION OF NITROGEN DIOXIDE AND α-PINENE

Residence time (hours)	NO_2 conc. (ppm)	α-Pinene conc. (ppm)	Diam. (micron)	Count (million particles/ft.^{3}) 0.3	0.5	1.0	1.8
1	1/2	1		2.492	.1931	.0077	.0000
1	1/4	1/2		.2603	.0042	.0000	
1	1/4	1/2		.4865	.0121	.0000	
1	1/8	1/4		.0191	.0000		
1	1/8	1/4		.0085	.0000		
1	1/16	1/8		.0041	.0000		
1	1/32	1/16		.0000			
2	1/4	1/2		1.155	.0441	.0008	.0000
2	1/4	1/2		.9697	.0110		
2	1/8	1/4		.0877	.0000		
2	1/16	1/8		.0807	.0000		
2	1/32	1/16		.0096	.0001	.0000	
2	1/16	1/32		.0000			
5	1/4	1/2		5.317	.7324	.0704	.0000
5	1/8	1/4		2.077	.1238	.0085	.0000
5	1/8	1/4		.5088	.0076	.0086	
5	1/16	1/4		.0818	.0013	.0000	
5	1/32	1/16		.0012	.0001	.0000	
8	1/16	1/8		.0817	.0028	.0005	.0000
8	1/32	1/16		.0523	.0025	.0004	.0000
8	1/64	1/32		.0011	.0000		

Reproducibility was only fair. Aerosol counts varied by a factor of two to four between duplicate runs.

Table 6 shows that aerosol can be formed in this system but only in large count at unrealistically high concentrations. Longer irradiation times promote greater aerosol formation but even for eight hours time the amount of aerosol formed was tiny at the lowest concentrations. It was apparent from these experiments that a realistic simulation of smog aerosol generation would require a far more sophisticated laboratory reactor design.

Additional experiments were done to test the idea that NO_3 might be able to oxidize SO_2 to SO_3:

$$NO_2 + O_3 \rightarrow NO_3 + O_2$$

$$NO_3 + SO_2 \rightarrow SO_3 + NO_2$$

$$SO_3 + H_2O \rightarrow H_2SO_4 \text{ (aqueous aerosol)}$$

The sulfuric acid should form as a countable aerosol. The reagents were mixed and given time to react, then the number of aerosol particles in the mixture was counted.

The stirred flow reactor (Figure 7) was used as the reaction vessel. The air that was used to dilute the reagents was purified passing through a heatless air dryer filled with charcoal. The air was then brought up to constant humidity by bubbling through distilled water immersed in an ice bath.

After a five-hour flush of the vessel with air, an aerosol count was taken with a 40-1 Bausch and Lomb counter to determine the background concentration of aerosol. This background varied from (0.0 to 0.2) $\times 10^3$ particles/cu ft. The background was not altered when NO_2 or O_3 were introduced into the vessel. Introduction of SO_2 did alter the background, so a filter was connected to the line that transfers SO_2 from its dispensing tank to the input manifold. All the reagents were stored in LPD tanks in which they were diluted with prepurified nitrogen.

At the start of the experiment the aerosol count was taken, then the reagents were mixed with an appropriate amount of air to give the desired concentrations. Nitrogen dioxide was measured colorimetrically using a spectronic 20 and Saltzmann's reagent. Ozone was measured with a Mast Ozone meter and sulfur dioxide with a conductivity analyzer. Because of mutual interferences in the analytical technique the individual reactants were added to a stream of clean air and their concentrations measured, then the three components were dispensed into the manifold.

Two experiments were run with a concentration of 1 ppm of all regents and 10 ppm of all reagents. Both times reactor output did not exceed the

background particle count. It can be concluded that SO_2 does not undergo oxidation to SO_3 under the condition of this experiment. Calvert and Heitpiss have reached the same conclusion.[13]

With this stirred flow system and purified air the PAN/SO_2 was reinvestigated. As before, aerosol could be produced by photolysis of this mixture but not in the dark. Neither this reaction nor the photodecomposition of PAN is understood. The absorption of near UV (about 3000) by PAN is quite weak and seems inadequate to account for the photolysis. This cannot be a firm conclusion until quantitative data become available on the strength of this weak UV absorption. The PAN/SO_2 experiment does demonstrate that this experimental system can produce an aerosol.

SECTION 6

FUTURE POTENTIAL

The techniques evolved under this program have good potential for further useful development. The infrared technique especially, if further developed, might be most useful. Its chief advantage is the possibility of obtaining unique information on such difficult aerosol components as sulfuric acid with the potential for distinguishing it from sulfates. Aside from a direct gas phase technique such as the spectrophone (not yet perfected) impaction onto a noble metal such as platinum offers less risk of sample transformation than any other technique. Its principal shortcoming is the lack of a quantitative calibration. The following developments might be investigated to improve the method:

1. Quantitative calibration of the infrared spectrum by sampling from a synthetic aerosol stream analyzed by some other method or by microanalysis of the impacted spot;
2. Improvement of the air environment during spectral recording by better CO_2 and water removal;
3. Improvement of the library of reference spectra by generation of better synthetic aerosols by either a) mixing acid gases such as sulfuric, acetic, etc. with basic gases such as ammonia or organic amines. This would permit inclusion of organic components b) photochemical aerosols generated in a smog chamber such as one of the two at UCR.

The impactor itself might be improved several ways:

a) Shorten the impaction slit to reduce the length of the sample to match the image in the reflector attachment. This would be especially valuable for sampling photochemical synthetic aerosols where sample volume is limited.

b) Impact on a small drum which could be turned stepwise every hour (as in the modification of the Lundgren impactor made by Cunningham at Argonne).

c) Better sample flow control and measurement using either a critical orifice or a surge tank or both.

Two "apparent" improvements that would probably not be worthwhile are:

a) Adding a third impaction stage for further size discrimination. This is based on the belief that particles large enough to impact have a bimodal distribution. The photochemical aerosol which is responsible for visibility loss is primarily in the diameter range below one or two micrometers and the soil dust is primarily in the larger size fraction.

b) Increase in resolution of the spectrum. Tests at EPA with Fourier interferometry indicate that there is no additional structure to be resolved. This is to be expected for these condensed phase spectra.

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